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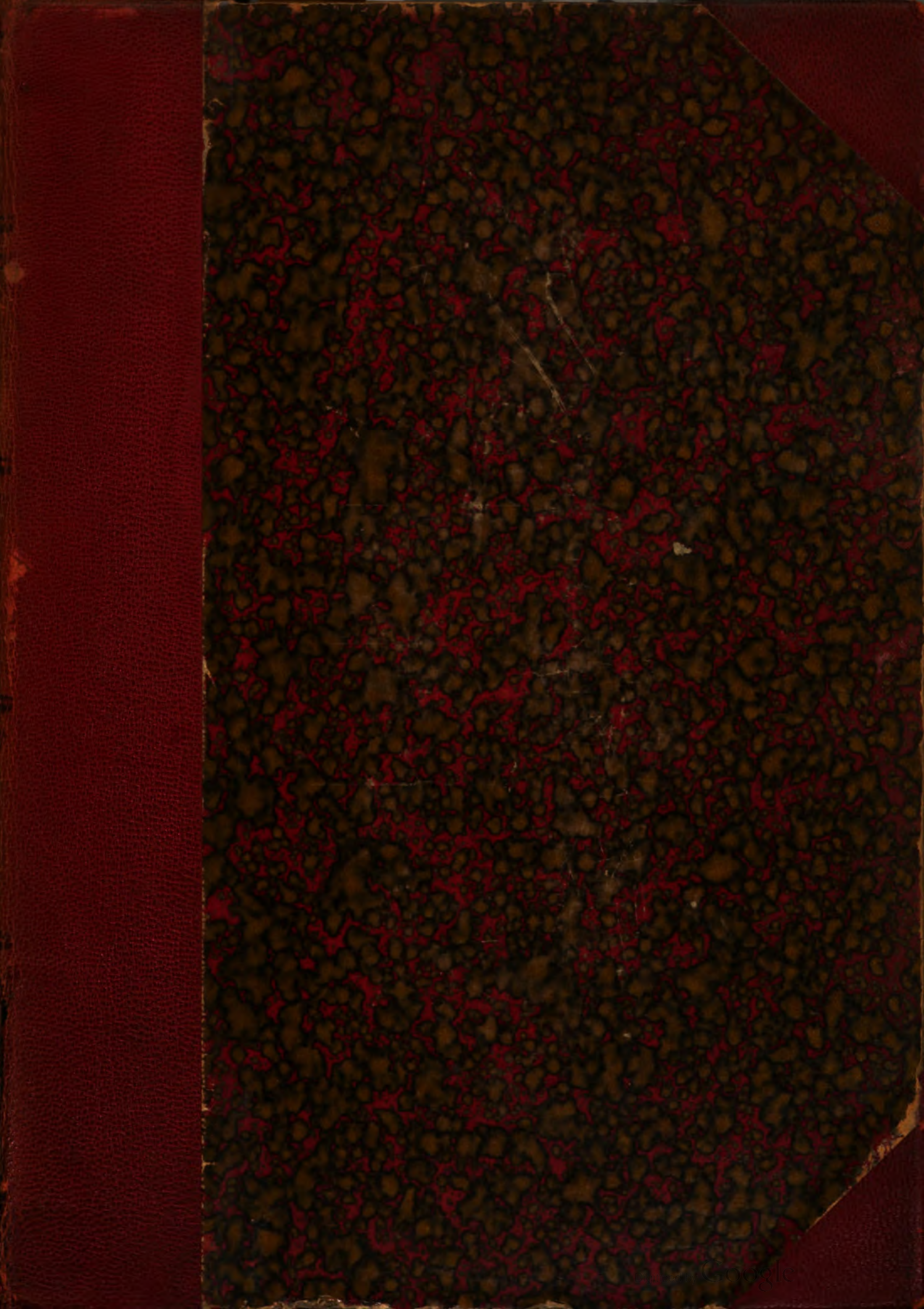

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BULLETIN

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

VOLUME 10

1914

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CONSTANTS OF SPECTRAL RADIATION OF A UNIFORMLY HEATED INCLOSURE, OR SO-CALLED BLACK BODY, I

By W. W. Coblentz

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I. INTRODUCTION

In the present research two distinct methods are employed in the investigation of the partition of energy in the spectrum of a uniformly heated inclosure or so-called black body. These methods employ (1) "isothermal" and (2) "isochromatic" energy measurements.

Owing to unavoidable delays in assembling all the apparatus for making the measurements at the highest temperatures, using a vacuum furnace, the intention of withholding[1] all the data until the completion of this investigation has now been abandoned. The present paper deals primarily with the form of the isothermal spectral energy curve, extending to about 6.5μ, and with the mathematical equation representing this energy distribution. An exact knowledge of the form of the spectral energy curve is necessary in order to determine whether the computations of the constants should be made on the basis of the Wien or the Planck equation. To obtain this isothermal spectral energy curve the temperature of the radiator must be kept constant while exploring the complete spectrum. In the isochromatic method, energy measurements are made in a selected region of the spectrum, using two or more different temperatures.

In a subsequent paper it is purposed to give what is hoped to be more precise values of the constants of spectral radiation, determined by the method of isochromatic energy curves (also isothermals, obtained with quartz and with fluorite prisms), which method apparently admits of a higher precision when the form of the energy curve, and hence the basis of computation have been established.

It has, of course, been realized all along that the method of obtaining the constants from the isothermal energy curves is subject to numerous difficulties, owing to atmospheric absorption in the apparatus. But it has favorable features not possessed by the method of isochromatics, and it is hoped that it will be possible to place the entire optical path and radiator in vacuo, in order to obtain the spectral energy curve free from atmospheric absorption bands. This will be the crucial test to determine the form of the energy curve. One of the causes of disagreement in the results obtained by present-day experimenters is owing to the method of computation (Planck or Wien equations) employed in the reduction of the observations. With the optical path in a vacuum there is no objection to having a focal length of several meters for the objective mirror, thus increasing the dispersion and hence removing one of the present objections to the use of a fluorite prism. This is especially desirable when working at high temperatures. Using a larger dispersion it will be possible to determine the constants with greater precision by both the isothermal and the isochromatic curves. This no doubt will require a redetermination of the refractive indices of fluorite.

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[1] As stated in J. Wash. Acad. Sci., **3**, p. 10; 1913. This is an abstract of the data and manuscript compiled to Dec. 12, 1912. The mean value of C as given here for the "1911" series is high, owing to the large percentage of curves that were observed at high temperatures where the correction for reducing the temperatures above 1400°, observed with a thermocouple, to the gas thermometer scale was about 4° larger than is employed in the present paper.

It may seem somewhat belated to question the prevailing notion that the form of the spectral energy curve has been thoroughly established. However, when one inquires thoroughly into the matter it is found that there is hardly a single piece of experimental work that stands the present-day criteria for deciding whether either one of the formulæ, Wien's or Planck's, fits the experimental observations. In the earlier work of Paschen,[2] the Wien equation seemed to agree with the experimental results. However, viewed from present-day experience this was probably owing to the lack of blackness of the radiators, and the presence of atmospheric absorption which would seriously affect the shape of his energy curves obtained at low temperatures (100° to 500° C).

The results published by Lummer and Pringsheim[3] showed that the theoretical formula of Wien did not fit the experimental curve and a more complicated formula[4] was published which fitted the experimental data at hand when using a certain dispersion curve of fluorite. This curve now appears to be incorrect; hence the formula is incorrect. In a subsequent paper they[5] tested the Planck as well as the Wien equation for the spectral region of 12μ to 18μ and concluded that neither of these formulæ fit the experimental observations. Subsequent to this work, Paschen[6] published data purporting to prove that the Planck equation fitted the observed energy curves, but, as will be mentioned elsewhere, this was made decisive by multiplying the observed curves, beyond 3.9μ, by arbitrary factors, which did not appear to seriously affect the computations of the constants. The comments made at that time, by Lummer and Pringsheim,[7] were to the effect that the results were not a satisfactory proof of the Planck equation.

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[2] Paschen: Sitzber. Akad. Wiss., Berlin, **21**, pp. 403, 959; 1899.

[3] Lummer and Pringsheim: Verh. Phys. Gesell., **1**, pp. 33, 215; 1899.

[4] Lummer and Jahnke: Ann. der Phys. (4), **3**, p. 283; 1900.

[5] Lummer and Pringsheim: Verh. Phys. Gesell., **2**, p. 163; 1900.

[6] Paschen: Ann. der Phys. (4), **4**, p. 277; 1901.

About the only precise work done at that period was that of Rubens and Kurlbaum,[8] who examined the residual rays (9 to 50μ) reflected from quartz, fluorite, and rock salt, the radiator being heated to various temperatures from $-188°$ to $+1500°$ C. They found a closer agreement between the experimental observations and the values obtained by computation using Planck's equation than obtained with any of the other formulæ tested, but there was not an exact agreement.

While the Planck formula was therefore fairly well proven experimentally for the extremely long wave lengths, and therefore presumably for the intervening spectral region, there was evidently room for experimental work on the determination of the exact form of the spectral energy in the region transmitted by a fluorite prism, viz, from the visible spectrum to 6μ in the infra-red.

The most definite statement that can now be made is that the Planck equation fits the experimental observations better than any other equation, which is also based upon plausible theoretical assumptions. But we do not know with certainty whether the theoretical curve will be found to coincide exactly with a perfect experimental energy curve. Planck's introduction of the expression $(e^x-1)^{-1}$ instead of e^{-x}, which occurs in the Wien equation, raises the emissivity on the long wave-length side of the spectral energy curve, thus bringing it closer to the observed curve. However, some of apparently the best experimental curves (judged by the method of computation of λ_m from equation (6) which should give uniform values) seem to fall somewhat below the theoretical, Planck curve, for the region beyond 5.5μ, just as though the true formula were something lying between the Planck and the Wien equations and having a factor, say $(e^x - 0.8)^{-1}$, instead of $(e^x - 1)^{-1}$. Just how much of this depression of the observed curve, below the theoretical curve, is caused by atmospheric water vapor can not be determined without an elaborate outfit from which the water vapor and air can be entirely removed. Not until then can this question of the form of the mathematical equation be definitely settled.

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[7] Lummer and Pringsheim: Ann. der Phys. (4), 6, p. 192 (see p. 210); 1901.

[8] Rubens and Kurlbaum: Ann. der Phys. p. (4), 4 p. 649, 1901.

II. SPECTRAL RADIATION FORMULAS AND METHODS OF COMPUTATION OF THE FORMULAS[9]

The great mass of theoretical speculations, now at hand, seem entirely out of proportion to the slender experimental data upon which they are based. It is therefore desirable to proceed to the discussion of the present experimental research without further reference to theory.

In the previous researches already cited the position of the maximum emission, λ_m, of an isothermal spectral energy curve appears to have been computed by taking the wave lengths, λ_1 and λ_2, corresponding to equal emissivities, $E_1 = E_2$, on the normal spectral energy curve. The formula used for computing λ_m is:

$$\lambda_m = \frac{(\log \lambda_2 - \log \lambda_1)\ \lambda_1\ \lambda_2}{(\lambda_2 - \lambda_1)\ \log e} \tag{1}$$

which is obtained directly from the Wien equation.

$$E_\lambda = c_1\ \lambda^{-\alpha}\ e^{-c/\lambda T} \tag{2}$$

The Wien displacement law, which is the mathematical expression for the shifting of the maximum emission toward the shorter wave lengths, with rise in temperature, is:

$$\lambda_m T = A \text{ (a constant).} \tag{3}$$

The important spectral radiation constant, in equation (2) useful in optical pyrometry, etc., is:

$$C = \alpha \lambda_m T \tag{4}$$

in which the value of $\alpha = 5$.

---

[9] In order to have a convenient and precise nomenclature, the following symbols are used: A for $\lambda_{max}\ T$; λ_m for λ_{max}; C for c_2 of former publications; σ for the coefficient of total radiation.

There are, of course, other methods for determining the radiation constant, *C;* but for the purpose of the present investigation it seemed better to obtain a great many computations of this constant, from the most reliable parts of an isothermal spectral energy curve (which is possible with equations (1) and (6)) than to attempt to determine *C* from a determination of the slope of an iso-chromatic curve. Isochromatic energy measurements were, of course, also made with the same apparatus, but fluorite is not well adapted for the purpose. Furthermore, since the computation of that data is incomplete, the discussion of the results will be given in a forthcoming paper, as already mentioned. At present this procedure of obtaining mainly isothermal curves seems the best that could have been followed, considering the difficulties which arise in operating a vacuum bolometer and maintaining it at a constant radiation sensitivity.

From the beginning it was found that, when computing λ_m by equation (1), the values usually decreased uniformly when λ_1 and λ_2 were taken at equal ordinates (emissivities, $E_{\lambda_1} = E_{\lambda_2}$) which were far apart, to a fairly constant value for λ_1 and λ_2 taken close together. This condition had not been mentioned by previous investigators. Hence, when the first announcement was made [10] of the progress in the present investigation (recorded in the present paper as "series of 1909") no values of the constants were given other than the general statement that the constant *A*, in equation (3) seemed to be as high as any value that had been published at that time. This high value, as is now evident, was owing partly to the method of computation by equation (1). There was also evidence that radiation could come from the cooler parts of the porcelain radiator, which became soft and sagged when operated at high temperatures. This would also tend to give too high values to the constants, and the work was undertaken anew.

It was then decided to compute the value of λ_m from Planck's equation

$$E_\lambda = c_1 \lambda^{-\alpha} (e^{c/\lambda T} - 1)^{-1} \tag{5}$$

on the assumption that the observed curve fits the theoretical curve, which is now found to be true for about 80 per cent of the experimental curves. The value of λ_m is easily derived[11] from equation (5) by equating $E_{\lambda_1} = E_{\lambda_2}$, and for the complete solution it is:

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[10] Amer. Phys. Soc. Proc., Apr. 26, 1909; Phys. Rev., 28, p. 466, 1909.

$$\lambda_m = \frac{\alpha(\log\lambda_2 - \log\lambda_1)\lambda_1\lambda_2}{\alpha'(\lambda_2-\lambda_1)\log e} - \frac{\lambda_1\lambda_2\left[\log\left(1-e^{-c/\lambda_1 T}\right) - \log\left(1-e^{-c/\lambda_2 T}\right)\right]}{\alpha'(\lambda_2-\lambda_1)\log e} \tag{6}$$

The second term in this equation can usually be abbreviated, since terms involving λ_1 are usually negligible. For values of λ_2 which are less than 4μ the term $\log\left(1-e^{-c/\lambda_2 T}\right)$ may be expanded into a series[12] and (by dropping all terms but the first) be used in the form $-e^{-c/\lambda_2 T}\log e$. In this equation $\alpha' = 4.9651$ and $C = \alpha^1\lambda_m T$. It may be noticed that an approximate value of C is necessary in order to obtain a solution for the second-term factors in equation (6). This may be obtained by solving for λ_m by using only the first term in equation (6). All the final results of the present research have been reduced by using a value of $C = 14500$ in computing the value of the second term in equation (6). However, in computing the λ_m from any spectral energy curve, a value of $C = 14\,400$ would decrease the mean value of λ_m by only about 0.005μ, for the temperatures at which the present investigations were made.

In case one can not observe the complete energy curve—as, for example, when using a quartz prism which absorbs heavily beyond 2.2μ—it is possible to compute the value of λ_m from the Planck equation by reducing the observed energy curve to the normal spectrum and taking from the energy curve the values of E_1 at λ_1 and E_m. The proper equation is:

$$\frac{E}{E_m} = \left(\frac{\lambda_m}{\lambda}\right)^5 \frac{(e^{4.9651}-1)}{(e^{4.9651\lambda_m/\lambda}-1)} \tag{7}$$

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[11] Phys. Rev., **32**, p. 591, 1911. Unfortunately, as first published (Phys. Rev., **29**, p. 553, 1909, and Jahrb. Radioaktivität, 7, p. 123; 1910), this solution contained numerous typographical errors. Although never so used, the second term was then published in a more symmetrical form, which is, however, more cumbersome for some methods of computation. The statement in a subsequent note (Phys. Rev., **31**, p. 317, 1910) that this method of computation is illusory in spite of its applicability is erroneous. After eliminating an error in the numerical calculations, this method of computation is now found to be the only one which gives concordant results.

[12] This is shown in a paper by Buckingham and Dellinger, this Bulletin, 7, p. 393, 1911. In practice, however, it is found that such approximate solutions are inadequate for wave lengths greater than 3.7 to 4.0μ, and there is but little time saved in so using the formula.

This equation appears to be well adapted when using a large dispersion, as, for example, when using a quartz prism; but the temperatures must be sufficiently high so that the E_m does not fall in the region beyond 2.2μ where quartz begins to absorb heavily. This equation is not well adapted to a fluorite prism, owing to the steepness of the energy curve on the short wave-length side, where one would want to use it, and also owing to the fact that, at the temperatures usually employed in the present research the E_m usually falls in the region of atmospheric absorption bands or in the region of 1.6μ where the dispersion curve of fluorite has a point of inflection. The latter, as explained elsewhere, makes it quite difficult to determine accurately the factors for reducing the observations from the prismatic to the normal spectrum. This equation has therefore not been used in computing λ_m from the curves obtained with the fluorite prism. With a larger dispersion, as already mentioned, equation (7) could be used as a check on equation (6).

For computing the constant, C, from an isochromatic energy curve, at any wave length, λ, Planck's equation was used in the following form:

$$c = \frac{(\log E_2 - \log E_1)\lambda T_1 T_2}{\log e(T_2 - T_1)} - \frac{\left(e^{-c/\lambda T_2} - e^{-c/\lambda T_1}\right)\lambda T_1 T_2}{T_2 - T_1} \tag{8}$$

where E_1 and E_2 refer to the emissivities corresponding to the temperatures T_1 and T_2, respectively. In this equation the terms $\log\left(1 - e^{-c/\lambda T_1}\right)$ etc., which are similar to the terms in equation (6) are expanded in series and only the first term of the expansion $\left(-e^{-c/\lambda T_1}\log E\right)$ is used. As in equation (6) an approximate value of $C = 14\ 500$ is used in applying the second term correction. For wave-lengths up to 1μ this correction term (to the Wien equation) is small, being only 2.1 and 4.3 for temperature intervals of $(T_2 - T_1)$ 363° and 623°, respectively, when using $T_1 = 1450$. However, these corrections increase very rapidly with wave length beyond 1μ, so that at 2μ, with the same temperature intervals ($T_1 = 1450$; $T_2 = 1813$ and 2073°) the corrections to the values of C amount to 168 and 227, respectively. This explains the rise in the value of C with wave length as found by Lummer and Pringsheim, who did not use the second term correction. Energy curves which coincide closely with the Wien equation would give uniform values of C with increase in wave length, when computed by using only the first term in equation (8), as was found by Paschen. In their preliminary results Warburg[13] and his assistants found that the value of C, obtained from isochromatics using a quartz prism, is independent of the wave length. On the other hand, they found an increase in C with wave length when using fluorite prisms.

A geometrical solution for λ_m proposed by Buckingham[14] was applied to the series of observations[15] recorded in this paper as the "Series of 1910." The computations, based upon this geometrical method for applying the second term correction factor in equation (6), do not differ much from the present computations in which the complete correction factor (second term in equation (6)) was applied. However, the geometrical method for applying the second term correction factor is not entirely free from arbitrary assumptions, so that all the herein-described observations were recomputed on the new basis of equation (6), with additional corrections for losses by reflection at the prism faces, and the fluorite window covering the bolometer. These additional corrections, occurring as they do on the short wave-length side of the energy curve, should and do give somewhat smaller values of λ_m for the 1910 series than was obtained by the approximate solution. The newly computed values of the 1910 series are in agreement with all the others, as now computed on the basis of the Planck equation. From the beginning it was felt of the greatest importance to obtain an extensive series of observations, under all sorts of conditions, leaving the exact computation of the results until the very last and then computing all the data on a uniform basis. From the results obtained this procedure seems amply justified. The fact that the numerical values of the constants are smaller than the older determinations of Paschen, and of Lummer and Pringsheim (and, for that matter, the earlier values of the present data, obtained by a different system of computation, and not including all the correction factors for reflection) need not disconcert us; for as noted elsewhere the older data are in agreement with the present values, when computed on the same basis. Ultimately it may be proven that the spectral energy curves fall between the theoretical ones represented by the Wien and the Planck equations which would give higher values to the constants. Only a determination of the complete spectral energy curves, entirely free from absorption bands, will decide this question. As already mentioned, this will require the placing of the entire optical system in a vacuum. In the meantime it is gratifying to note that from 75 to 80 per cent of the spectral energy curves, obtained in the present investigation, are found to fit the Planck equation within the experimental errors of observation.

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[13] Warburg, Hupka, and Müller: Zs. Instrk., **32**, p. 134; 1912.

[14] Now incorporated in a paper by Buckingham and Dellinger, this Bulletin, **7**, p. 393; 1911.

[15] Phys. Rev., **31**, p. 317; 1910. Jahrb. Radioaktivität und Elektronik, **8**, p. 1; 1911. The mean value of energy curves gave a value of $\lambda_m = 2944$.

Other criteria might have been used to test the validity of the Planck equation; for example, the increase in the maximum emission ($E_m = BT^{\alpha}$) with rise in temperature. But this involves uncertainties owing to the maximum emission shifting into atmospheric absorption bands, variation in the radiation sensitivity of the apparatus, etc. Furthermore, it puts the burden of the proof upon the temperature and not the radiation measurements. The computation of λ_m by equation (6) is less arbitrary, for it permits the selection of the best parts of any given energy curve, where there are no absorption bands; and the number of computations on any curve is limited only by the patience one has in making them. It certainly speaks well for the method (by equation (6)) that values λ_m computed from values of λ_2, extending from 2.5μ to 5.5μ, are in agreement to 1 part in 200, as was often found when the energy curves were sufficiently free from absorption bands to permit computation in the doubtful region at 2.5μ. No computations were made by bridging over absorption bands, and then reading values of λ_1 or λ_2 falling therein. Owing to the great number of energy curves, most of which have been recomputed and redrawn during the past six months, it was not possible to spend any length of time in studying the curves. This might have produced a series of values which differ less from the mean value. However, the great mass and diversity of the material obviates the personal bias which can so easily, though unconsciously, enter work of this type.

III. SUMMARY OF PREVIOUS INVESTIGATIONS

In spite of all that has been published on the partition of energy in the spectrum of a black body there is but little experimental data at hand which is more than qualitative in value.

Paschen[16] observed an extensive series of spectral energy curves at temperatures ranging from 100° to 450° C, using six different kinds of bolometers covered with different kinds of absorbing material, e. g., lampblack and platinum black or copper oxide; also having the bolometers in the focus of a hemispherical mirror. The radiators were heated by means of boiling water, aniline, sulphur, etc. The mean value of all his observations, which are in close agreement, was $A = 2890$. He continued the work at temperatures ranging from 400° to 1050° C using a large porcelain radiator. He used also metal cups of copper or platinum blackened with oxides of copper or iron, and heated within this porcelain radiator, making in all about a dozen different arrangements of the radiators. The bolometer was covered with platinum black and was situated in the focus of a hemispherical mirror to "blacken" it. The mean of the new series was $A = 2907$, with a probable error of ± 16. The mean value of all his work up to this time is about $A = 2900$, and since the contours of his energy curves were supposed to fit the Wien equation ($\alpha = 5$) the value of C is 14 500. In the meantime Lummer and Pringsheim (their work will be discussed presently) came to the conclusion that the Wien equation did not fit their experimental results. Paschen[17] thereupon undertook the work anew, after redetermining the reflecting power of silver and the refractive indices of fluorite. He used a porcelain tube radiator, also three other radiators which he blackened as in the preceding research. He took the wise precaution to project an image of the radiating wall of the black body upon the spectrometer slit in order to avoid possible radiations from the side walls and diaphragms falling upon the prism and bolometer. He made complete corrections for the selective reflection of the silver mirrors and also for the loss by reflection from the prism. He then found that his observations fitted neither the Wien nor the

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[16] Paschen: Sitzber, Akad. Wiss. Berlin, **21**, pp. 403, 959; 1899.

[17] Paschen: Ann. der Phys. (4), **4**, p. 277; 1901.

Planck equation, the values on the long wave-length side of the energy curves falling between the two theoretical curves. He found that if (for reasons he himself could not explain, loc. cit., p. 295) he multiplied his observations by factors varying from 1.02 at 3.91μ, 1.038 at 4.59μ, 1.050 at 5.12μ, 1.068 at 6.26μ, 1.195 at 8.25μ, etc., the observed energy curve would fit the Planck equation and fulfilled better the condition of congruence. Upon this basis, and presumably by computing the λ_m by using equation (1), he obtained a value of $A = 2921$ for his newest data. He then applied factors to some of his previous data, thus making them agree better with the Planck equation and the value of A was increased from 2890 to 2915, or about 0.87 per cent. From this it appears that, if he had not multiplied his observations by these arbitrary factors, his latest results would have been about 0.87 per cent lower or $A = 2900$, which is practically the same as the value previously obtained.

TABLE 1

Data from Paschen

Temp. absolute	λ max. (Wien eq)	λ_m T	λ^1 max. (Planck eq)	λ^1_m T
	μ		μ	
1580.6	1.846	2918	1.837	2903
1567.9	1.858	2913	1.850	2901
1357.4	2.157	2929	2.150	2918
1352.7	2.159	2920	2.152	2911
1347.4	2.172	2927	2.164	2916
1337.4	2.188	2926	2.180	2916
1055.2	2.777	2929	2.769	2922
1053.7	2.770	2919	2.762	2910
1052.2	2.781	2926	2.774	2919
875.0	3.328	2911	3.319	2904
876.4	3.333	2914	3.324	2913
Mean..........	....	2921	....	2912±5

$C = 14,458 \pm 25$

We can obtain a further and more plausible estimate of the correction to Paschen's values by applying the values of the second term which result from computing λ_m by equation (6) in the present research. This is admissible because his observed curves are said to fit the Planck equation to about 4μ. His energy curves can not, therefore, differ much from those obtained in the present research for the spectral region up to 4μ. Proceeding on this basis the values of λ'_m (see column 4) in Table 1 were obtained by multiplying Paschen's values of λ_m (column 2) by 1.007 (i. e., α/α') which transfers them from the Wien to the Planck system of computation. From these new values of λ_m were deducted the second term factors of equation (6), which were obtained from the computations of the spectral energy curves, observed at closely the same temperatures in the present research. The second term correction factors were taken from computations in which λ_2 fell in the region of 3.4 to 3.9μ, where the value of λ_m, as computed from the present research by using the first term in equation (6), has closely the same value as published by Paschen. The minimum value of this second term factor for this spectral region varied from 0.022μ at the highest temperatures to 0.033μ at the lowest temperatures. However, second term corrections which are 5 to 10 per cent higher would not seriously affect (decrease) the results. Column 4 of Table 1 therefore gives a fair estimate of the values of λ'_m, on the basis of computation required by Planck's equation. This gives a mean value of $A = 2912$ and $C = 14\,458$, which is close to the value obtained by the rough estimate of the correction, and it happens to be the same as found in the present experiments.

Since the original values at long wave lengths were arbitrarily changed by Paschen to fit the Planck curve, the writer feels justified in attempting to reduce the data in this manner by the methods involved in the present research. On this basis, and with the clue that the curves fitted the Planck equation to about 4 μ, it appears that, if Paschen had used the present system of computation, his value of C would be of the order of $C = 14\,458$.

The most reliable values of the constants published by Lummer and Pringsheim[18] require a treatment similar to that just given to Paschen's data. They used the earlier indices of refraction of fluorite, published by Paschen[19] in 1894, which are in error in wave length by 0.02 μ for the region of 1 to 2.5 μ. But little information is at hand as to how they obtained their values of λ_m. In their earlier work they say that, after bridging over the absorption bands by means of a smooth line, the values of λ_m and E_m may be read directly from the spectral energy curve.[30] Making the corrections to their values λ_m (column 4, Table 2), which, as already stated, are too large by about 0.02 μ at 1.7 to 2.7 μ, owing to a wrong calibration curve for the fluorite prism, their mean value of A is reduced from 2940 to 2930. Their curves did not fit the Wien equation, and the Planck equation was not yet published in its complete form when they made known their results. From the present research, using similar radiators of their design under similar conditions, it is evident that their energy curves can not be markedly different from these obtained by the writer. Their curves should therefore be reduced by the present system of computation in order to make the constants comparable with the values obtained in the present research. This was accomplished by multiplying their corrected values of λ'_m by 1.007 ($=\alpha/\alpha'$) and by applying the second term correction of equation (6). The values of A obtained by the system of computation which is required by Planck's equation, are given in column 5 of Table 2. The mean value is $A=2911$ and $C=14\ 450$. If we exclude the last value of $A=2814$, which is evidently not comparable with the

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[18] Lummer and Pringsheim: Verh. Phys. Gesell., Berlin, **1**, p. 215, 1899.

[19] Paschen, Ann. der Phys. (3), **53**, p. 301, 1894; (4), **4**, p. 299, 1901.

TABLE 2

Data from Lummer and Pringsheim

Temp. absolute	λ max. (Wien eq)	λ_m T	λ^1max. (Planck eq)	λ^1_m T
	μ		μ	
1646.0	1.78	2928	1.745	2871
1460.4	2.04	2979	2.010	2933
1259.0	2.35	2959	2.301	2896
1094.5	2.71	2966	2.690	2943
998.5	2.96	2956	2.945	2940
908.5	3.28	2980	3.260	2961
723.0	4.08	2950	4.050	2927
621.2	4.53	2814	4.530	2814
Mean..........	....	2940	....	(2911) 2924±8

C=14,518±40

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[30] Lummer and Pringsheim: Verh. Phys. Gesell, 1, p. 33, 1899.

rest, the mean value is $A = 2924$ and $C = 14\ 518$. They made no correction for loss by reflection from the silver mirrors and from the prism, which would be most effective in shifting the energy curve on the short wave-length side of the maximum toward the visible spectrum, and would still further decrease their value of C by 0.3 to 0.4 per cent. Hence, a fair estimate of the constant as obtained by Lummer and Pringsheim is $C = 14\ 460$ to $14\ 470$. Since their porcelain tube radiator was supported only at the ends and hence would bend in the middle when heated above 1200°, and since this radiator was placed directly before the spectrometer slit (judging from the writer's experience with a similar outfit), it was impossible to be certain that no radiation came from other parts of the black body than the central radiating wall of the tube. Radiation from the cooler diaphragms tend to give too large a value of λ_m for the temperature indicated by the radiating wall.

Unfortunately none of their original observations were published. Values for a few points of two spectral energy curves were published[21] in comparing the experimental results with theoretical values computed by various radiation formulæ. Constructing the curves for these two series of data (temperatures 1259° and 1646° Abs.; for the latter the data is insufficient to draw a good curve) the values of A were computed by the present system, equation (6). This gave $A = 2890$ and $A = 2920$, respectively, and a mean value of $C = 14\ 430$. However, since so few observations were at hand to draw the curves, and since the energy curve at the lower temperature fitted best the Wein computation for λ_m, and since the energy curve for 1646° seemed to fit neither the Wein nor the Planck system for computing λ_m, no great reliance is placed on this computation.

To the writer it seems that all this data should be considered from the standpoint of historical interest, since it seems impossible to give it much weight in connection with the results obtainable at the present day. All the work done in recent years is found to be at variance with the uncorrected results of Paschen, and of Lummer and Pringsheim. The first intimation of this fact came from a research by Holborn and Valentiner[22] in the visible spectrum.

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[21] Lummer and Jahnke: Ann. der Phys. (4), **8**, p. 283, 1900.

[22] Holborn and Valentiner: Ann. der Phys. (4), **22**, p. 1, 1906.

They found a value of $C = 14\ 200$. Recently Valentiner[23] has corrected this value for lack of blackness of the radiator, arbitrarily raising the value to $C = 14\ 350$.

The investigations by Warburg[24] and his assistants is not yet published in complete form. The preliminary data for isochromatic curves gives a value of $C = 14\ 380$ and for isothermals $C = 14\ 360$. In the latter the range is from $C = 14\ 230$ to 14 480. Considered as a whole, a fair estimate of the results of the foregoing investigations indicate a value of $C = 14\ 400$ to 14 460.

IV. APPARATUS AND METHODS

Under this title are given only the main outlines of the instruments used in this research. For a more complete description it is necessary to consult the original papers to which frequent reference is made.

1. Bolometer and Galvanometer.—For the first part of this investigation an air bolometer was used, which was placed at the focus of a hemispherical glass mirror, 5 cm in diameter and having an opening 0.5 by 1.5 cm at the center. The most of the observations were made with a vacuum bolometer, known as bolometer No. 10, placed at the focus of the hemispherical glass mirror just mentioned. The sensitive platinum strips of the bolometer were 10 by 0.6 by 0.0003 mm, the resistance of each strip being 5.6 ohms. The resistance of the complete bolometer was 8.9 ohms (depending of course upon the battery current and the vacuum) with a temperature coefficient of 0.023 ohms per degree. The galvanometer resistance was 5.09 ohms at 20° C, with a temperature coefficient of 0.0194 ohms per degree. It was usually operated on a complete period of three to five seconds, and sensitivity of 2 by 10^{-10} ampere.

The rear side of each bolometer strip was bright, and the front side was painted with a mixture of lampblack and platinum black, then smoked with soot from a paraffin candle. The fluorite window was covered with thin sheet copper, which was painted with lampblack, and which formed a knife-edge slit, from 2 to 3 mm in width, for admitting upon the bolometer the part of the spectrum which was to be measured. The rear wall and tube leading to the viewing window of the glass vacuum chamber was painted with lampblack to absorb or diffuse any radiation which passed by the bolometer strip. A more detailed description of the radiometric apparatus has already been published,[25] and for clearness the vacuum bolometer is illustrated only by a simple diagram in Fig. 1.

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[23] Valentiner: Ann. der Phys. (4), **39**, p. 489, 1912.

[24] Warburg, Leithauser, Hupka, and Müller: Zs. Instk. **32**, p. 134, 1912. As this paper goes to press a recent communication (Sitzber Akad. Wiss. Berlin, I, p. 35, 1913) gives what appears to be a final value of $C = 14\ 374 \pm 40$ and $A = 2894 \pm 8$.

The reflecting power of lampblack and of platinum black have also been published.[26] The results show that the reflecting power of lampblack and of platinum black is low and fairly uniform through the spectrum. The amount lost by diffuse reflection from the bolometer would be returned upon its path owing to the presence of the hemispherical mirror.

A large glass bottle of about 4 liter capacity prevented a noticeable change in the gas pressure, resulting from leakage, and more especially from a change in vapor pressure with temperature of the material used in cementing the joints of the vacuum bolometer. Since a quite accurate knowledge of the bolometer resistance is required, the gas pressure was reduced to only about 0.2 mm (cathode dark space 3 to 4 mm) at which pressure the bolometer resistance is still quite independent of the degree of evacuation.

The sensitivity of the bolometer-galvanometer was varied by means of a resistance box R_2 (see wiring diagram, Fig. 1) placed in series with the galvanometer. By this means the galvanometer deflections (maximum allowed was 12 to 14 cm) were kept within the range of proportionality with the current flowing through the galvanometer. In previous papers[26a] it was shown that the galvanometer deflections were proportional to the current for deflections up to 20 cm; also that the galvanometer deflections were proportional to the energy falling upon the bolometer strip for intensities far exceeding those to which the bolometer was exposed in the present research. This is of importance in connection with the question of the constants, observed at high temperatures.

A standard resistance of 100 000 ohms was kept in parallel with one branch of the bolometer, see Fig. 1, S_1. By short-circuiting 20 000 ohms of this resistance the current in the bolometer circuit

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[25] This Bulletin, **4**, p. 392, 1908; **9**, p. 7, 1912 (vacuum bolometer).

[26] This Bulletin, **9**, p. 283, 1913.

[26a] See note 25, p. 17.

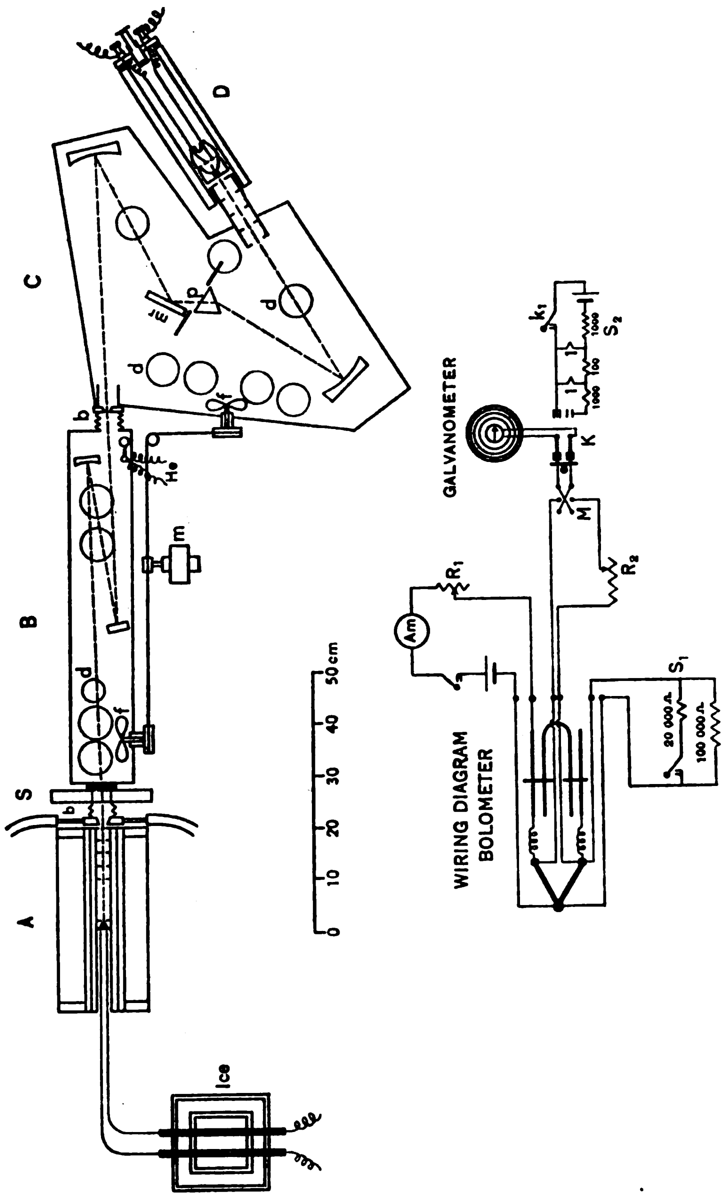
A
S
B
C
D
b
d
f
m
He
p
m
Ice
0
10
20
30
40
50cm
WIRING DIAGRAM
BOLOMETER
GALVANOMETER
Am
R₁
R₂
M
K
k₁
S₁
S₂
20 000 Ω
100 000 Ω
1000
100
1

Fig. 1

was unbalanced, causing a galvanometer deflection which was used as an arbitrary standard for testing the electrical sensitivity of the bolometer-galvanometer circuit. The galvanometer sensitivity was tested by throwing the switch K (Fig. 1) to the right and closing the switch K_1, through the battery of S_2.

No standard was provided for testing the radiation sensitivity (which varied with the gas pressure) owing to the difficulty in proving a standard radiator which could be easily operated in the spectrometer. The main test of the radiation sensitivity of the instruments was a repetition of the observations which had been made at the beginning and during the series of observations. The bolometer was usually operated on a constant current of 0.03 ampere, and it was usually found that if the galvanometer sensitivity remained constant the radiometric observations could usually be repeated to 1 part in 200. After exhausting the air the tendency of the radiation sensitivity is to slowly decrease. The electrical test of sensitivity using the standard resistance S_1 was, of course, frequently applied while observing a spectral-energy curve. Usually the galvanometer sensitivity[27] would remain constant throughout a series of observations on an energy curve, which required from one to one and one-half hours. During the first year's work, however, when an air bolometer was used, it required from two to three hours to observe a complete energy curve, and much difficulty was experienced from variation in sensitivity of the galvanometer, which required a complete period of six to seven seconds in order to attain a sufficiently high sensitivity. At that time from 15 to 20 galvanometer readings, at any given spectrometer setting, was required to obtain a reliable mean value. With the bolometer in vacuo the same precision was attained in 5 to 6 readings of the galvanometer, which, owing to the high radiation sensitivity of the bolometer, could be operated on a complete period of four to five seconds. Usually about 30 spectrometer settings and from 200 to 250 galvanometer readings (including the repetitions) were required to obtain a complete energy curve. Hence, a conservative estimate of the total number of deflections recorded during the past four years is in excess of 40 000 observations.

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[27] In the afternoon the galvanometer sensitivity would increase 1 or 2 per cent and return to its original intensity the following morning, owing probably to the diurnal variation of the earth's magnetic field.

The present apparatus is the result of experiments extending over at least five years, during which time the radiation instruments have undergone repeated alterations and have been tried out on various subsidiary problems. The energy curves are not perfectly satisfactory, however, and, as is mentioned elsewhere, they probably never will be until the complete optical path is inclosed in a vacuum to eliminate atmospheric absorption bands.

In observing galvanometer deflections there is constantly a fluctuation in the readings amounting to 0.1 to 0.5 mm, whether or not there is a resistance in the galvanometer circuit for reducing the large deflections obtained when exposing the bolometer to intense radiation. The precision is therefore usually no higher for high than for low intensities, i. e., for large (reduced by resistance when being observed) or for small deflections. The proper method when using high intensities is to compensate the deflections by means of some sort of potentiometer device and reducing the operation to a null method, or at least to compensate for the greater part of what would be the true galvanometer deflection and read only the residual deflection. In this manner the aforementioned errors would be only in the residual deflection. However, such a device may contain other inherent errors, and in view of the great variation in the intensities measured, it did not seem justifiable for this part of the research to depart from the well-tried bolometric method of observing the direct galvanometer deflection. When operating the radiator above 1100° it was an easy matter to reduce the aforementioned fluctuations in the galvanometer readings by reducing its sensitivity; and with a galvanometer (complete) period of only four to five seconds a precision of 1 part in 200 to 300 could easily be attained. It is, therefore, an open question whether at these temperatures a greater precision could have been attained by null methods. In fact, considering the numerous other difficulties and the time saved, it is doubtful whether anything would have been gained by using other than the direct galvanometer deflection method of observation.

2. **Spectrometer.**—The spectrometer, from Fuess, was remodeled to suit the present investigation. The mirrors were 10 cm in diameter and 52 cm in focal length. An optically plane mirror 10 by 5 by 0.8 cm was mounted upon an especially constructed prism table. With the prism it formed the well-known Wadsworth method for maintaining minimum deviation.

The spectrometer circle was divided to 10′ with a glass vernier, which read directly to 1′. The micrometers for measuring angles to less than 1′ were never used; for the bolometer was purposely constructed to subtend 4′ of arc (the spectrometer slit and bolometer strips were 0.6 mm wide) and the spectrometer settings were made to the even minutes of arc. This was done to simplify the reduction of the data to the normal spectrum, before any of the observations were plotted for computing the constants.

The mirrors were silvered by the Brashear process and polished with the finest optician's rouge. The whole optical system, Fig. 1, was inclosed in a box of thin sheet copper, with three openings in the top, which gave access for removing and adjusting the mirrors. Although the silver mirrors could be kept an indefinitely long time in this box without tarnishing,[28] they were silvered at the beginning of each year's work.

The lids covering these openings were closed with soft wax. Within the box, in line with, but below the optical path, were numerous large glass dishes *d*, *d*, containing fresh phosphorous pentoxide, while other vessels contained freshly broken sticks of caustic potash. The vessels not below the optical path were wrapped in black velvet. Small fans, *f*, *f*, Fig. 1, driven by a motor, *m*, were operated, before starting a series of observations, in order to dry the air.

The experimental work was planned for the winter months when the humidity was low. This was as important as the air stirring and the drying devices. The water vapor can be reduced to a fairly low value with drying material; but the carbon dioxide can not be thoroughly eliminated. There is also evidence that the absorption bands of oxygen[29] at 3.2μ and 4.7μ may cause quite an appreciable depression in the energy curves. Lummer and Pringsheim (loc. cit.) mentioned such an absorption band but did not know what substance caused it. It may have been caused by hydrocarbon vapors; but owing to the long optical path (about 2.5 m) from the radiator to the bolometer it seems more probable that atmospheric oxygen exerts an appreciable absorption.

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[28] This Bulletin, 7, p. 197; 1911 ("Preservation of Silver Mirrors").

[29] Investigations of Infra-red Spectra, Carnegie Publication, No. 35, p. 49; 1905. Subsequent observers have not found these bands in oxygen.

The entire interior of the spectrometer box was, of course, painted with lampblack in a dilute alcoholic solution of shellac, to absorb scattered light.

The spectrometer arms were set so that the rays fell upon the collimating mirrors at as small an angle of incidence as was possible, when in connection with the bolometer. The astigmatism was therefore very small, and it was not increased a measurable amount by increasing the angle of incidence upon the mirror, which occurs in rotating the prism table in order to project the infra-red spectrum upon the bolometer strip. This might be of importance when using a slit image which covers the whole length of the bolometer strip, as was done in some of the present work; but by actual measurement it was found that this possible source of error, if present at all, was negligible.

3. **Prisms and their Adjustment.**—The greater part of the work was done with a flawless fluorite prism (No. 1) having a refracting angle of 60° and circular faces 33 mm in diameter. Although this prism seemed to belong to the green variety of fluorite it was practically colorless and entirely free from internal cleavage planes. An examination of the transmission of samples of light green fluorites [30], which contained appreciable coloring matter showed that it is highly improbable that this prism has any absorption bands, which, if present, should occur at 1.5μ and 3μ. The possible absorption bands of fluorite would be extremely weak, and they would occur (e. g., the 3μ band) in the region of atmospheric absorption bands, where no computations were made. There was also available a large prism, No. II (refracting angle 60°; faces 52 by 50 mm) which belonged to the purple variety of fluorites. It was colorless but contained numerous internal cleavage plates which scattered much light. It will be shown that, probably as a result of this scattering, only about 25 to 30

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[30] This Bulletin, **9**, p. 116; 1912.

per cent of the observed spectral energy curves fitted the Planck equation, when about 80 of the energy curves produces by the small prism, operated under similar conditions, fitted the Planck equation. The other prisms used in the latest work will be described in a forthcoming paper. The face of the prism *p*, Fig. 1, was covered with a diaphragm of cardboard, painted with lampblack, which prevented radiations (other than those entering the prism) from passing beyond the central part of the spectrometer box.

All the adjustments were made with the prism mounted upon its table. This includes the adjustment of the prism to the vertical axis of the spectrometer, the adjustment of the prism faces to parallelism with the auxiliary mirror *mr*, Fig. 1, the measurement of the angle between the prism face and the mirror; and the angular setting necessary to cause the light to pass through the prism at minimum deviation.

The method is fully described elsewhere[21] and is too lengthy to repeat here. In order that all the rays may pass through the prism at minimum deviation, the angle of incidence must vary as the rays fall upon the auxiliary silver mirror *mr*, Fig. 1. The angle between the mirror and the adjacent prism face is about 80°. On a subsequent page it will be shown that the correction for variation of the reflecting power with angle of incidence is negligible.

The alignment of the radiator and the adjustment of the mirrors in the box *B*, Fig. 1, so that in projecting an image of the radiating wall *d*, Fig. 2, upon the spectrometer slit the spot of light passes centrally through the prism *p*, Fig. 1, is extremely delicate, and at the beginning of each new series of observations (as well as during the observation of an extensive series of energy curves) the spot of light coming from the radiator, heated to 1250 to 1300°, was adjusted to pass accurately through the central part of the prism. The importance of this is evident from the fact that the spot of light was about 27 mm. in diameter while the prism was only 33 mm. in diameter, so that any slight lateral displacement of the image falling upon the spectrometer slit was liable to throw the light partly off the prism face. After the light had passed through the prism the spectrum was adjusted upon the bolometer strip by means of the adjusting screws which are attached to the intervening mirror.

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[21] Investigations of Infra-red Spectra, Carnegie Publication No. 35, p. 18; 1905.

4. **Radiator or so-called Black Body.**—The unmounted porcelain tubes *A*, *B*, *C*, in Fig. 2 were purchased abroad, which explains much of the delay in concluding this investigation, owing to the difficulty in promptly obtaining the proper material. The outer porcelain tube *C*, Fig. 2, was surrounded with a ring of asbestos cloth, and the intervening space was filled with fine magnesium carbonate, which, however, on heating was partly decomposed into the oxide and had to be refilled several times during the first part of the work. The ends were of kaolin.

The outer heating tube *B* was 5.7 cm in diameter. It was wound with a strip of platinum 0.02 mm in thickness and 1 cm wide, and after some usage was fastened permanently within the tube *C* by means of kaolin. This part of the radiator was used throughout the work. To aid in temperature compensation the platinum ribbon was closely wound at the ends with only a few turns in the center.

The inner tube *A*, which was 3 cm in (internal) diameter, had to be removed frequently in order to repair the platinum winding, to be replaced by another tube when broken and to facilitate adjustments, etc. The ends rested upon porcelain rings in order to keep the proper adjustments, and when once in place for a series of observations the open spaces between the tubes *A* and *B* were closed with a thick paste of kaolin, sectioned radially to allow for expansion, shrinkage, etc. This tube was uniformly and closely wound with a strip of platinum 0.01 mm in thickness. The distance between the successive turns of platinum ribbon was of the order of 0.3 to 0.5 mm, so that the porcelain was almost entirely covered with metal. The width of the strip was 2 cm at the center and decreased uniformly to 1 cm width at the ends as shown in Fig. 2. It required about 220 cm of platinum ribbon cut in this manner to cover the inner tube.

In the earlier part of the work attempts were made to regulate the temperature uniformity by varying the heating current in the two coils, *A* and *B*, by means of separate rheostats in the circuit with the two windings of these two porcelain tubes. It was found,

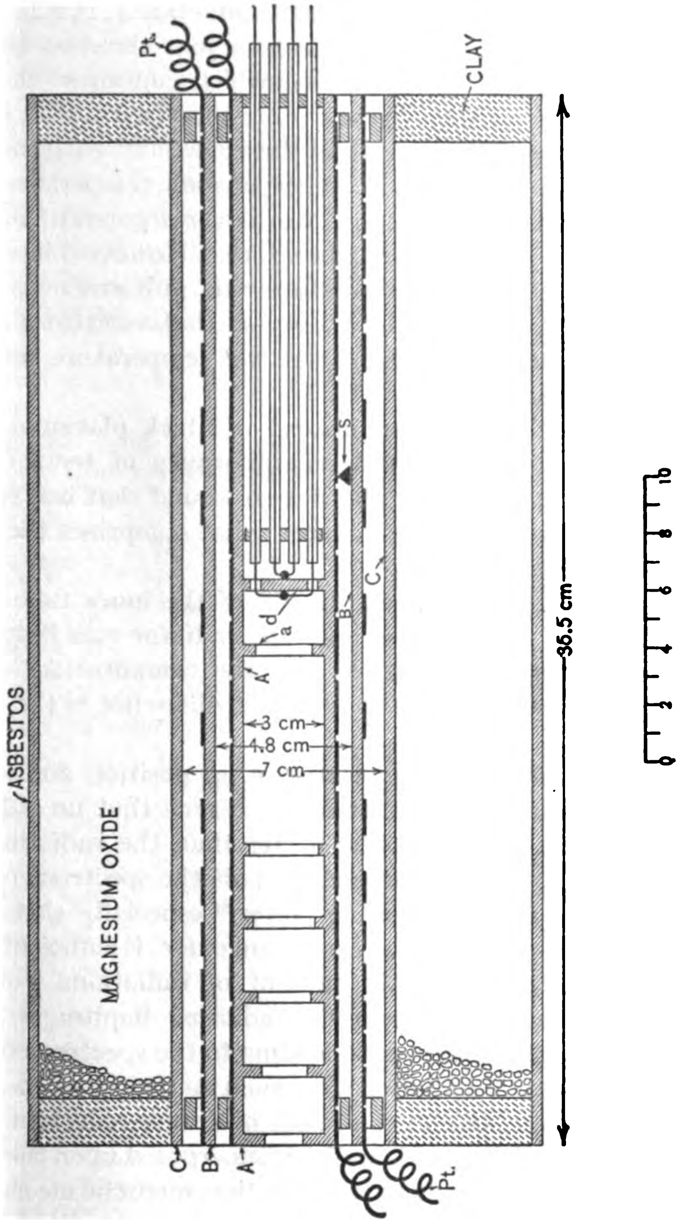
Pt.
CLAY
S
C
B
d
a
A
3 cm
4.8 cm
7 cm
ASBESTOS
MAGNESIUM OXIDE
36.5 cm
C
B
A
Pt.
0
2
4
6
8
10

Fig. 2

however, that at the high temperatures used, the heating by radiation was far more effective than heat conduction. It was found more satisfactory (and less laborious) to join the two heating circuits in parallel with the main line, which contained the rheostats, and allow each tube to take its proportionate part of the current than to attempt to regulate the current in each radiator by means of separate rheostats. Hence, at some temperatures the radiators were at a uniform temperature over a greater length of the tubes than at a different temperature. However, it will be shown presently that the temperature was uniform over a far greater length than required by theory so that variations in the length of the radiator over which there was temperature uniformity is of minor importance.

The use of platinum ribbon instead of thick platinum wires eliminates the question of local nonuniformity of temperature. The central 2.5 cm length of tube was so wound that one turn of the platinum ribbon entirely covered what comprises the theoretical black body.

On several occasions the heating coil of the inner tube broke during a series of observations, and the radiator was heated by radiation from the outer coil, *B;* but the computations of the energy curves do not indicate a systematic difference in the values of the constants.

The construction of the apparatus, e. g. position and size of opening in the water-cooled shutters, was such that no radiation from the side walls, which may be hotter than the radiating diaphragm, *d*, Fig. 2, could be projected upon the spectrometer slit. Furthermore, the diffuse reflecting power,[32] especially that of the radiators painted with cobalt or chromium oxide, is sufficiently low so that only an imperceptible amount of radiations from the hotter side walls, which fall upon the radiating diaphragm, *d*, will be reflected upon the optical path leading to the spectrometer slit. In measuring the total radiation from such an inclosure, the extra amount of radiation, which (as a result of diffuse reflection of the radiations from the hotter side walls) is superposed upon the radiations from the diaphragm under investigation, might be measurable. But after dispersing these radiations into a spectrum it would be a hopeless task to attempt to detect the increase in emissivity, at any spectral region, which might be caused by the superposition of diffusely reflected radiations from the side walls upon the radiations emitted by the diaphragm.

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[32] This Bulletin, 9, p. 283, 1913.

The radiating diaphragm was 30 mm in diameter, but the arrangement of the collimating mirrors, *B*, Fig. 1, was such that the image of only about 18 mm of this diaphragm was projected upon the spectrometer slit. The spectrometer slit was 10 mm in height, so that only the radiations from about 10 mm of the central portion of the radiating diaphragm entered the spectrometer. It was only by this arrangement that consistent results were obtainable.

TABLE 3

Showing the Drop in Temperature Within the Radiator at Different Distances from the Radiating Wall; a Rise in Temperature is Indicated by a Plus Sign

Distance from radiating wall; cm	0 to 0.5	1	2	3	4	5	6	8	10	12
Temp. centigrade of radiating wall	Drop in temperature									
I 612°	0°	0	0	....	0	....	0.5	4.3	13.5	....
980	0.3?	0	0	....	+1.5	....	+0.8	4.0	....	....
1225	0	....	0	....	0	....	0	6.2	18	....
1275	0	....	....	0.1	....	....	0	6.0	....	....
1283	0	....	....	....	....	....	0.6	1.2	....	....
1300	0	....	0.5	....	1	....	2	7	20	....
II 910°	0	....	+0.6	+0.5	0	....	1	4	....	....
975	+0.6	....	+1.7	....	+1.3	....	0	3	....	....
1147	+0.6	+1.1	+0.8	....	....	1.3	2.2	6	9	....
III (Marquardt) 950°	0	....	0	....	....	0	....	....	0?	16

In the first work, "Series of 1909," the radiator was directly before the slit, as used by Lummer and Pringsheim. This, of course, reduced the length of the optical path and hence atmospheric absorption, but it was impossible to be certain that no radiations other than those from the diaphragm could enter the spectrometer slit. This was especially true for the first part of this series when following the custom of previous investigators; no attempt was made to prevent the inner tube, *A*, Fig. 2, of the radiator from sagging, which occurs when heated to 1200°. The fragment of porcelain, with a knife-edge, *s*, Fig. 2, about 2 mm long, was used to prevent the inner tube from sagging. It was placed about 2.5 to 3 cm to the rear of the radiating diaphragm. No local cooling could be detected as the result of its presence. This support was one of the chief factors in the successful operation of the radiator. In fact the success attained in the present research is owing to three things, (1) the introduction of a support to prevent sagging, (2) more thorough insulation of the thermocouples by enlarging the holes in the radiating wall to cover the thermocouples with thicker-walled porcelain tubing; this (3) permitted the use of blackened radiators.

The length of porcelain tube between the radiating wall and the first perforated diaphragm, *a*, Fig. 2, was about 2.5 cm. After the experience gained in winding the first radiators, there was no difficulty in spacing the compensation coil and cutting the platinum ribbon of the inner heating coil so that, at all temperatures, there was a uniformity in temperature to 0.5° for a distance of 6 cm or more from the radiating diaphragm and a drop in temperature of only 10 to 18° at a distance of 10 cm in front of the radiating wall. In the second "Series of 1909," after rewinding the furnace, the temperature of the air, at a distance of about 2 cm from the radiating wall, was about 1.5 to 1.8° higher than the temperature of the diaphragm.

In these tests for temperature uniformity within the radiator it is to be remembered that the experiments were made with (1) the exploring thermocouple drawn through a small hole in the radiating diaphrahm, and (2) by inserting the thermocouple, inclosed in thin porcelain tubes, through the opening in the front of the radiator. In using the latter method there was evidence showing that the drop in temperature was partly owing to a cooling of the radiator by the removal of the thermocouple. Series III of Table 3 was made on a Marquardt porcelain tube by method (1) using a thermocouple of wires 0.1 mm in diameter, and the temperature was found uniform for a distance of 12 cm from the radiating wall, where it suddenly dropped 16°. The small fluctuations in temperature uniformity may be due, in part, to lack of homogeneity in the exploring thermocouple.

From the fact that the radiator was heated to a uniformity of 1°, over three times the length of the theoretically perfect radiator, it appears as though a uniformly heated inclosure had been attained to a sufficiently high degree of accuracy for the work at hand. By cutting the platinum wire much narrower at the ends the temperature compensation could have been produced over a greater length of the radiator, but there appeared no advantage radiometrically, by so doing. On the other hand, it would have been disadvantageous in quickly heating the radiator to have the platinum cut much narrower at the ends; for, owing to the low heat conductivity of the porcelain, it would become overheated at the ends when starting, and the tube would break or its outer surface would crack. As used, the temperature of the radiator could be raised to 1500° in less than three hours without danger of breaking the porcelain tube. It was found, however, that, after a tube had been heated 25 or 30 times, the platinum seemed to shrink into the porcelain, causing a pinkish colored compound which, on account of its different expansion coefficient, would chip loose and, by warping, would tear the platinum ribbon.

The radiating diaphragm was adjusted and focussed upon the spectrometer slit by inserting into, and illuminating, the interior of the inclosure by means of an especially prepared Nernst glower, 1 cm long, which was operated on a transformer. In this manner, especially when using unblackened tubes, there was no difficulty in making these adjustments. On interchanging radiators, tube *A*, Fig. 2, and before making any adjustments, or after making a series of observations, the image of the center of the thermocouple was always found to be within 1 mm of the center of the slit. The water-cooled shutter was then secured in place and the adjustments tested. This glower was, of course, removed before making observations. The radiator had, of course, to be adjusted so that the light fell centrally upon the prism face. This was accomplished by heating the radiator to 1200° to 1300° and adjusting the optical bench upon which it rested. The adjustments were also tested by sending the light from a Nernst glower through the spectrometer in the reverse direction. For this purpose the viewing microscope was removed from the bolometer, *D*, Fig. 1, and the light from a Nernst glower was passed along its axis. This of course produced a spectrum, part of which passed through the spectrometer slit and from thence passed out into the radiator. With a right-angled prism or mirror it was possible to determine the accuracy of the adjustments upon the diaphragm; or with the inner tube, *A*, Fig. 2, removed it was possible to adjust the axis of the radiator. These various adjustments were preliminaries, and as already mentioned the final adjustment was made by heating the radiator to a high temperature and tracing the spot of light emanating therefrom through the entire apparatus.

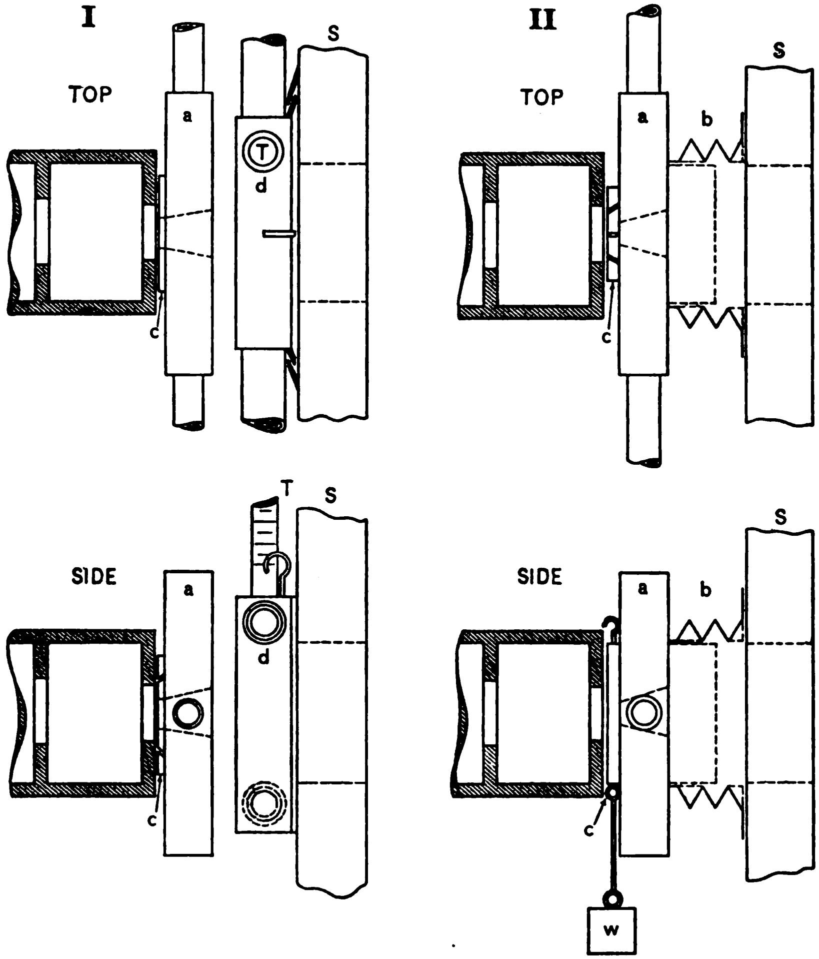

Fig. 3

5. **Water-Cooled Shutters.**—Two different types of water-cooled shutters were used in this investigation. The first type, "shutter No. 1," shown in Fig. 3, I, consisted of a large stationary copper shield, *S*, 1 cm in thickness and 5 by 50 cm in area which was filled with water. To this shield, was attached a shutter, *d*, of thin sheet copper, 5.5 by 6 in area and 1 cm in thickness, which could be raised or lowered in front of the opening in the shield, *S*, thus admitting radiation into the spectrometer. This shutter contained a thermometer, *T*, and through it a stream of water was kept flowing. The temperature of the water flowing in the shutter, *d*, varied from 6 to 15°, depending upon the temperature of the radiator and the outside air. Water was also kept flowing through the shield, *a*, which was 6 cm in diameter and 1 cm in thickness. This shield contained a slot into which was slipped thin brass plates, *c*, having openings varying from 3 to 6 mm. After the black body radiator had been adjusted to the spectrometer, the shield, *a*, was clamped firmly in front of the opening in the radiator. This outfit was used on "Series of 1909" where the black body stood directly in front of the spectrometer slit. The shutter, *d*, was also used with a similar shield *S*, of somewhat smaller dimensions, Fig. 1, in "Series IX, 1912." However, it permitted too much (humid) air to enter the spectrometer case, hence it was discarded. The second type of shutter, Fig. 3, II, consisted of a stationary shield, *S*, of thin copper, 40 by 20 and 1 cm thickness, shown at *S* in Fig. 1, which was filled with water. Water was kept flowing through the smaller shield, *a*, which was 6 in diameter and 1 cm in (internal) thickness. After the radiator was adjusted, this shield, *a*, was centered before the opening and rigidly clamped at a distance of 2 or 3 mm from the end of the radiator. As a further precaution this shield was fastened to the end of the black body radiator by means of plaster of Paris. The shutter, *c*, consisted of a sheet of brass about 1.2 mm in thickness and 2 by 1 cm in area which moved in vertical ways close against the water-cooled shield, *a*. It therefore had very closely the temperature of the shield, which as in shield No. I varied from 6 to 15° C. The shutter, *c*, was raised by means of a cord and pulley, as shown in the photographic illustration, Fig. 5, accompanying this paper, and, owing to the friction in the slots

required a small weight, *w*, to be attached permanently to cause it to return, by gravity. The knife-edge hole, *d*, in the diaphragm, *a*, was 4 mm in diameter, which, by the geometrical construction of the apparatus, did not permit radiations from the side walls to fall upon the spectrometer slit. The two shields, *S*, and *a*, were connected with a flexible leather bellows, *b*, which prevented air from passing into the spectrometer box. It avoided also jarring and displacement of the adjustments by expansions and contractions in the radiator. The shutter, *a*, was placed as close to the radiator as the expansion of the porcelain tube would permit, and the intervening space was packed with asbestos. By opening this shutter only when observations were made, it was possible to reduce the humidity of the inclosed air in the spectrometer box and keep it fairly constant while making observations. No attempt was made to keep a record of the temperature of the thin metal shutter, *a*, for it never differed sufficiently from the bolometer to enable one to detect experimentally radiations passing to or from the bolometer. Any corrections that would have to be made to the spectral energy curves, owing to an exchange of radiations between the shutter and the bolometer, would fall beyond 6μ, while the computations of the present research usually do not extend beyond 5.8μ.

6. **Temperature Scale and Temperature Measurements.**—The temperature of the radiator or so-called black body was determined by means of two Heraeus thermocouples of *Pt* and *Pt* + 10 per cent *Rh*. One of the thermocouples was placed horizontally across and in contact with the front side of the radiating diaphragm of the black body, as shown in Fig. 4, *A*, which is a section viewed from above. The lead-wires passed out through the rear of the radiator to the ice box, Fig. 1. In the "Series of 1912" when the inner walls and the front side of the radiating diaphragm were painted with chromium oxide or cobalt oxide, which becomes electrically conducting at 1200°, the front thermocouple was completely inclosed in a porcelain insulating tube, as shown in Fig. 4, *B*. The short piece of porcelain which lies across the radiating wall of the black body was covered with cobalt oxide. Since the cobalt oxide did not adhere well to the porcelain tube, the latter was first covered with a thin layer of iron oxide, obtained by wetting the

porcelain tube with writing ink which was burned into the tube. The cobalt oxide paint was then applied and also burned upon the tube by means of a blast lamp. After replacing the thermocouple inclosed in this short tube within the radiator the whole interior was again painted with a mixture of cobalt and chromium oxides. In order to be able to insert the thermocouple including the short tube, and also to paint the interior of the radiator, the first diaphragm (which in the commercial porcelain tube has an opening of only 1 cm) was removed, Fig. 4, *B*, and after making all the adjustments, another porcelain diaphragm was put in its place.

The cobalt oxide has a high temperature coefficient of absorption, so that it appears black on slight heating. Its emission spectrum [23] is continuous so that there is less difficulty in producing a perfect radiator than when the radiating inclosure is of white porcelain.[24] However, porcelains having a low melting point when heated above 1000° emit a far more continuous spectrum than the "Marquardt porcelain" from which are made the black bodies ordinarily used.

All these tubes, especially the painted ones, become electrically conducting when heated above 1300°, so that for higher temperatures the radiator was heated by alternating current from a motor-generator which was operated from a storage battery. By this means there was no more difficulty in maintaining a constant current than when heating the radiator directly by means of current from a storage battery. By means of a low resistance rheostat at the observing table, the current could be regulated so that the temperature of the radiator could be kept constant to a few hundredths of a degree. No observations were made, especially at high temperatures, when the temperature fluctuated as much as 0.1° from the mean value at which the radiator was being operated.

The temperature of the front side of the radiating wall was regulated by the heating current and the temperature of the rear side of the radiating wall was brought to that of the front side by changing the size of the opening, Fig. 4, at the rear end of the radiator. This was done by means of asbestos fiber. The amount of adjustment of the opening had, of course, to be regulated at every heating of the radiator, and also during a series of observa-

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[23] Investigations of the Infra-Red Spectra, No. 97, p. 120, Carnegie Institution of Washington, 1908.

[24] This Bulletin, 9, p. 81; 1912. (See p. 106.)

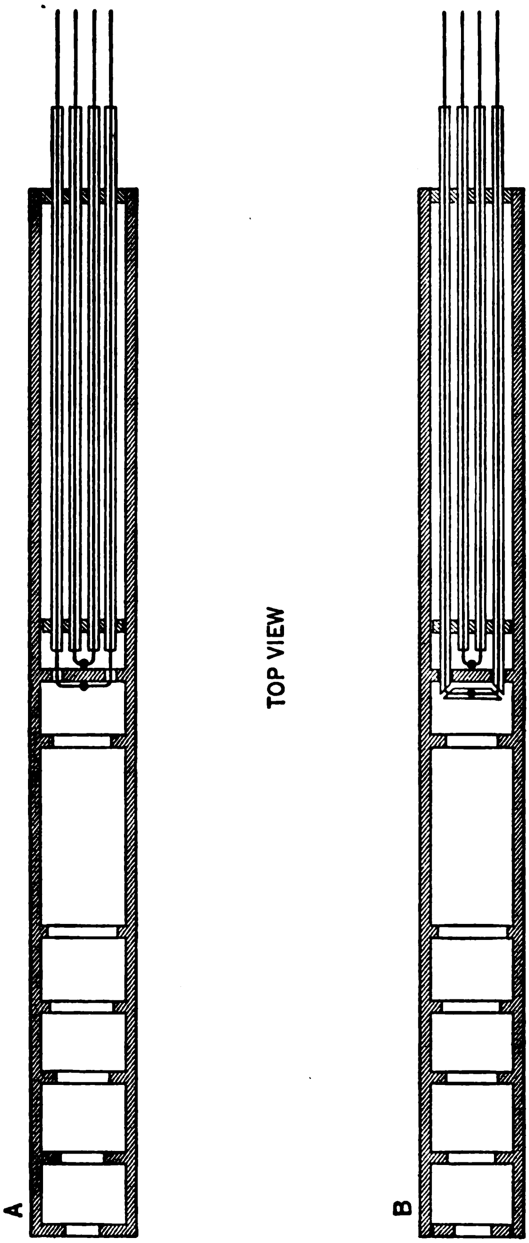

Fig. 4

tions. This was entirely a matter of experience and there was no difficulty in keeping the temperature difference of the two sides of the radiating diaphragm to within a few tenths of a degree. It was then assumed that the true temperature of the radiating diaphragm was that measured by the thermocouples; and it was felt that the temperature measurements were as well known as is the temperature scale. It is to be noticed, however, that the temperatures used fall well within the region of the known temperature scale. An error of 1° or 2° in the measurements of the temperature would mean an accuracy of 1 to 2 parts in 1400 to 1800, which is a far greater precision than is possible with the other measurements involved in the experiments.

The thermoelectric measurements were made by means of a potentiometer and a standard cell, both of which were standardized by the Electrical Division of this Bureau at the beginning of a series of measurements.

The thermocouples were frequently standardized by the Heat Division of this Bureau, by determining their emfs at the freezing points of zinc (419.°2), antimony (630.°0), and copper (1083°). From these emfs and temperatures the calibration curve was computed by the formula

$$E = a + bt + ct^2$$

This is the thermoelectric scale which on extrapolation beyond 1400° differs from the optical scale [35] based on the Wien equation using $C = 14\,500$ (i. e., differs from the thermodynamic scale) by the amounts given in Table 4.

TABLE 4

Temperature on thermoelectric scale	1200 C	1300	1400	1500	1600°
Optical—Thermoelectric (mean values)	0	2	6	14	25
Optical—Thermoelectric used by W. W. C.	0	0	1	7	18

The temperature scale used in the present investigation, for temperatures above 1400°, is the Optical Scale [36] which is obtained by adding to the thermoelectric temperatures a proportionate amount of the corrections given in the lower line in Table 4. This correction is somewhat smaller than given by Waidner and Burgess, owing to the fact that their corrections relate to the mean values of five different thermocouples. The emfs of the thermocouples used in the present research correspond very closely with the thermocouple, P_3 (used by Waidner and Burgess), which indicated temperatures 5 to 7° higher than the mean value. Hence the corrections (which become operative at 1400° C.) to reduce the observed temperatures to the optical scale are smaller by 5 to 7°, depending, of course, upon the temperature. The correction is quite large at 1500°, which may account for some of the high values of the constant, *C*, which still appear to be a trifle larger at high temperatures than at low temperatures. However, this occurrence of high values of *C* at high temperatures is not sufficiently systematic for the observations on different years to conclude that it is owing to this correction to the temperature scale (i. e., thermocouple readings reduced to the gas scale) or to a deviation of the observed curve from the Planck equation, but is the result of other experimental errors. In future work it is purposed to calibrate the thermocouples by using the melting point of palladium as the highest fixed point, thus eliminating this correction. This correction is of minor importance since but few energy curves were obtained at temperatures higher than 1400° C., and hence can not affect the mean value of the present results. The correction has no effect whatever upon the data obtained in 1912 (which is the crucial work), and ordinarily it might have gone unmentioned.

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[35] Waidner and Burgess; this Bulletin, 3, p. 205, 1907, Table 20.

[36] Modified as explained in the text; for, using the unmodified factors, the values of $\lambda_m T$ show an abnormal and systmatic increase in value at temperatures higher than 1400° C. We are therefore forced to choose between the possibility (1) that this variation is owing to the failure of Planck's law at high temperatures or (2) that, for the particular thermocouples used in this research, the given correction factors for reduction to the optical scale are too large. The writer has chosen the latter conclusion, and the result-obtained at high and low temperatures are now in agreement.

7. **Description of the Assembled Apparatus.**—In Fig. 5 is shown a photograph of the radiometric apparatus as used in the latter part of the investigation. The essential parts of the apparatus are shown in Fig. 1. Beginning at the extreme left of the plate, the double-walled ice box, *I*, contained the cold junctions of the thermocouples. The radiator is at *A*, and is shown in more detail in Fig. 2. An inner platinum-wound tube (broken) is shown at *Pt*. The main rheostats are at *R*, and the ammeter is shown at *Am*. The water-cooled shutter and the water-cooled diaphragm are shown at *S*, Figs. 1 and 4.

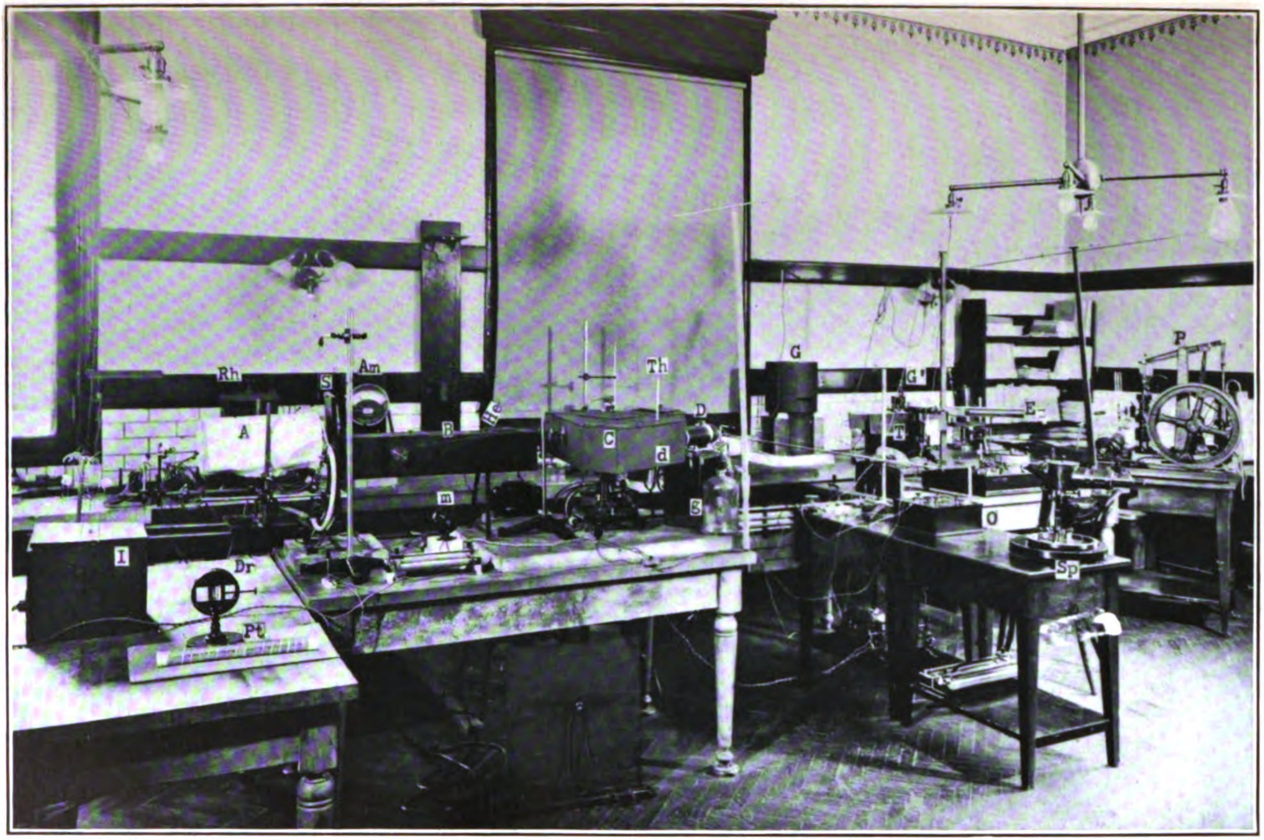
Rh
S
Am
A
B
He
C
Th
D
d
m
g
G
G'
T
E
P
O
Sp
I
Dr
Pt

Fig. 5.—*Radiometric laboratory.*

The air-tight metal box, *B*, contains a plane mirror and a concave mirror (5 cm in diameter, 50-cm focal length) for focusing the radiating diaphragm (*d*, Fig. 2) upon the spectrometer slit. It contains also glass dishes with dry potassium hydroxide and phosphorus pentoxide. The helium tube, *He*, can be rotated about a vertical axis so that it comes in front of the spectrometer slit. The tube is excited by a 2000-volt transformer situated at *t*, and the air is agitated by fans (*f*, *f*, Fig. 1) operated by a motor, *m*.

The spectrometer, with its optical parts inclosed in an air-tight metal box, is shown at *C*. The glass dishes containing phosphorus pentoxide are below the optical path and in the metal boxes, *d*, the bottoms of which may be unscrewed to renew the phosphorus pentoxide. The three lids on top of the spectrometer box admit adjustment of the optical parts. They are closed with universal wax. A thermometer is shown at *Th*. The spectrometer circle is viewed by means of a telescope, *T*, and is rotated by a lever, both of which are situated on the small observing table, *O*. The spectrometer and the radiator are joined to the box, *B*, by means of flexible leather bellows (*b*, *b*, Fig. 1), which prevents any strain acting upon the spectrometer arm.

The vacuum bolometer is within the metal case, *D*. For clearness of illustration the Geryk oil pump, used in evacuating the bolometer, was placed at *P*. When in operation it is joined to the large glass bottle, *g*, which is in series with the bolometer. The bolometer is kept balanced by rotating the light metal arms which extend to the observing tables, *O*. The auxiliary galvanometer inclosed in its iron shields is shown at *G*. It is mounted upon a massive wall-bracket upon which is placed a heavy slab of marble.

Upon the large observing table, *O*, are situated a telescope and scale, *T*, for reading the galvanometer, *G*; a potentiometer (the auxiliary moving coil galvanometer is at *G'*) and illuminated scale, *E*; and mercury switches leading to the thermocouple wires (shown strung across the room to the ice box, I). Upon the small observing stand are mercury and knife switches which are accessory to the bolometer and its galvanometer; also a telescope for setting the spectrometer circle and a dial resistance in series with the galvanometer, *G*. On the lower shelf of this table is shown the standard 100 000-ohm box, and a low resistance, *r*, which is used in regulating the electric current used in heating the radiator, *A*, and maintaining it at a constant temperature. The water-cooled shutter is opened and closed by means of a cord which passes over the pulley at *S*. By means of these devices the observer, at *O*, was able to control all the operations necessary in order to obtain a spectral energy curve. These operations included testing of the galvanometer-bolometer sensitivity, balancing the bolometer, setting the spectrometer circle, maintaining the radiator at a constant temperature, reading the galvanometer deflections, etc.

The mounting for the hemispherical mirror used in an investigation of diffuse reflection [37] is shown at *Dr*. The short-focus spectrometer used in photographing the light of the firefly,[38] and for obtaining spectral energy curves [39] in the visible and ultra-violet parts of the spectrum is shown at *Sp*.

The multiple sectored disk [40] (without its motor) previously described is shown at *Sd*.

8. **Refractive Indices Used for Calibration.**—Until within the past four years there was a wide discrepancy in the indices of refraction of rock salt and of fluorite, as determined in Europe and in this country. The foreign investigators using mirror spectrometers of about 35 cm focal length and bolometers subtending an angle of 3 to 6′ of arc attempted to attain an accuracy which they supposed far outweighed the precision attainable by Langley and Abbot with their spectrobolometer, which had a focal length of 2.3 meters and subtended an angle of 7″ to 1′.3. In this particular kind of work "size is a most important element of accuracy." [41]

The explanation of this discrepancy was finally obtained in 1908, when Paschen [42] published a redetermination of the indices of refraction of rock salt, which are in perfect agreement with the values obtained by Langley. This gave a clue to the discrepancy in the refractive indices of fluorite. Langley and Abbot had found the refractive indices of fluorite indirectly by comparing bolographs of the solar spectrum which had been obtained by means of the two kinds of prisms. Therefore Paschen's refractive indices of flourite should agree with those obtained by Langley and Abbot. Applying the correction for temperature coefficient [43] to Paschen's most recent determinations of the refractive indices of fluorite,[44] which are considered the most reliable, it was found that his values

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[37] This Bulletin, **9**, p. 283, 1913. J. Franklin Inst., **1**, 74, p. 549; 1912.

[38] This bulletin, **7**, p. 243; 1911.

[39] Publication No. 164, Carnegie Institution of Washington, 1912.

[40] This bulletin, **7**, p. 243; 1911.

[41] Langley: Annals Astrophys. Obs., vol. 1, p. 222; 1902.

[42] Paschen: Ann. der Phys. (4), **26**, p. 120; 1908.

TABLE 5

Refractive Indices, n, of Fluorite at 20°; Data from Langley and from Paschen

Wave length	n	Log n	Wave length	n	Log n
0.5893	1.43390	0.1565180	2.6519	1.42019	.1523455
.6562	257	.1561158	2.700	.41988	.1522517
.6867	200	.1559430	2.800	923	.1520528
.71836	157	.1558126	2.850	890	.1519518
.76040	101	.1556426	2.9466	823	.1517467
.8840	1.42981	.1552783	3.050	1.41748	.1515169
1.000	896	.1550200	3.098	714	.1514114
1.100	834	.1548316	3.241	600	.1510900
1.1786	789	.1546948	3.400	487	.1507134
1.250	752	.1545822	3.5359	376	.1503788
1.3756	1.42689	.1543905	3.8306	1.41119	.1495855
1.4733	642	.1542474	4.000	.40963	.1491051
1.5715	596	.1541073	4.1252	847	.1487476
1.650	558	.1539916	4.250	722	.1483620
1.7680	502	.1538210	4.400	563	.1478710
1.840	1.42468	.1537173	4.600	1.40355	.1472279
1.900	439	.1536274	4.7146	233	.1468502
1.9153	431	.1536046	4.800	130	.1465311
1.9644	407	.1535313	5.000	1.39900	.1458177
2.0626	357	.1533789	5.3036	9522	.1446427
2.1608	1.42306	.1532232	5.8932	1.38712	.1421141
2.250	258	.1530758	6.4825	7821	.1393154
2.3573	198	.1528920	7.0718	6805	.1361020
2.450	144	.1527272	7.6612	5670	.1324838
2.5537	080	.1525329	8.2505	1.34440	.1285290

fall exactly upon the dispersion curve of fluorite published by Langley.[45] Hence, for the region of the spectrum to 3.5μ to which Langley's work applies, the curve (Pl. XXVI *B*, loc. cit.) of refractive indices, which represents the observations of both observers, was adopted in the present research. This is a large plate, and the refractive indices are drawn to a scale of 1 mm = 0.002μ. Beyond 3.5μ Paschen's refractive indices were employed. The values adopted in computing the calibration curve used in the present research are given in Table 5. The necessity of this high accuracy arises in computing the slit-width correction for reducing the observations from the prismatic to the normal spectrum.

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[43] Micheli: Ann. der Phys. (4), 7, p. 772; 1902. Liebreich: Verh. Phys. Gesell., 18, p. 1; 1911.

[44] Paschen: Ann. der Phys. (4), 4, p. 302; 1901.

[45] Langley: Annals Astrophys. Obs., Smithsonian Institution, vol. 1, p. 222, Plate XXVI, B; 1902.

The value of the refractive index for λ = 0.58932μ was adopted from a consideration of the observations of Stefan, Sarasin, Pulfirich, Simon, Carvallo, Martens, and Paschen. The values of these various observers differ but little from the adopted value, the greatest difference amounting to perhaps 5″ in the minimum deviation of the D-lines of sodium.

That high precision was attained in the present calibration is evident from the fact that, by a single measurement, the intense emission line of helium[46] was located at λ = 1.084μ. The mean value of a large number of determinations by Paschen[47] using a large grating is λ = 1.083μ.

A variation in temperature of 1° causes a change in refraction of about 1″.75 in a fluorite prism. The experiments of Micheli and Liebreich (loc. cit.) show that the temperature coefficient of refraction is quite constant for the infra-red region of the spectrum concerned in the present investigation, so that the correction for change in dispersion is negligible. The essential requirement is to maintain an accurate setting of the bolometer upon the sodium lines, the "zero setting."

The calibration was computed for 20° C, and since the temperature within the spectrometer box departed only about 1° from this value, no correction is necessary to the observed data.

9. **Fiducial Reference Lines.**—The position which the bolometer occupies in the spectrum is determined from the calibration curve computed from the minimum deviation settings on the spectrometer circle, and the corresponding wave lengths. These minimum deviation settings are computed from a knowledge of the angle of the prism and the values of the refractive indices just discussed. The fiducial reference line, the "zero" of the spectrometer circle, is the sodium line λ = 0.5893μ. For convenience this "zero" of the spectrometer circle is set at some whole number, say 10° 0′

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[46] This Bulletin, 9, p. 81, 1912. (See p. 95.)

[47] Paschen: Ann. der Phys. (4), 27, p. 537, 1908.

0″, and the sodium line is caused to fall upon the bolometer strip. If the temperature changes appreciably during the observations the refraction of the prism changes noticeably and the sodium line will no longer fall upon the bolometer strip when the "zero setting" is at 10°. This was the method used for checking the adjustment at the beginning and end of every series of observations. The bolometer was provided with a micrometer screw[48] for making this adjustment.

The use of the sodium lines, $\lambda = 0.5893\mu$ as a standard of reference was inconvenient, and the more intense yellow helium line $\lambda = 0.5876\mu$ was adopted for the "zero setting." Repeated tests during the past five years failed to indicate an error as great as 5″ in setting the bolometer on these lines. The helium tube was pivoted so that it could be swung in front of the spectrometer slit, as shown in Figs. 1 and 5. .

10. **Corrections for Selective Reflection.**—The radiations from the black body are reflected five times at silvered surfaces and must pass through the fluorite prism and the fluorite window covering the bolometer. Experiments made by Paschen and by the writer show that the transmission of white fluorite is uniform throughout the spectrum to about 7μ, so that there is no correction for absorption in fluorite. In this research there are three corrections to the spectral energy curves: (1) A correction for variation in the reflecting power (R_1) of the fluorite surfaces (four in all, R^4_1), which is a function of the wave length and the refractive index; (2) a correction for the variation in reflecting power (R_2) with variation in angle of incidence upon the prism face (two reflections, R^2_2); and (3) a correction for the variation in the reflecting power (five reflections, R^5) of silver with wave length.

The value of R_1 was computed by the well-known Fresnel formula; $R_1 = [(n-1) \div (n+1)]^2$ using the refractive indices given in Table 5. The values are given in Table 6. The correction for variation in the reflecting power (R_2) with angle of incidence upon the prism face was computed from the Fresnel formula:

$$R_2 = \frac{I}{I_0} = \frac{1}{2}\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{1}{2}\frac{\operatorname{tang}^2(i-r)}{\operatorname{tang}^2(i+r)}$$

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[48] See Fig. 9, this Bulletin, 4, p. 439; 1907.

where *i* = angle of incidence and *r* is the angle of refraction. For minimum deviation $r_1 = r_2 = \alpha/2$ where α is the refracting angle of the prism.

The correction for the variation in the reflecting power of silver, with variation in the angle of incidence, was investigated [49] and found to be only 0.12 per cent per degree of angular rotation for angles of incidence between 54° and 64°. Since the total angular rotation in passing from 1μ to 6μ is less than 4° this correction is negligible. As already mentioned the whole optical system being inclosed and the moisture eliminated, the silver mirrors could be kept indefinitely. However, they were silvered each year, at the beginning of a new series of observations.

TABLE 6

Showing the Variation in Reflecting Power, R_1, of Fluorite with Refractive Index, n; and R_2, with Variation in the Angle, i, of Incidence

λ	$R_1=\left(\frac{n-1}{n+1}\right)^2$	$(100-R_1)^4$	i		R_2	$(100-R_2)^2$	$\frac{(100-R_1)^4}{(100-R_2)^2}$
μ		Per cent	°	′		Per cent	Per cent
0.360	0.0332	87.37	46	16.7	0.0442	91.36	79.80
.397	.0328	.52		8.7	.0436	.47	80.07
.486	.0322	.72	45	56.3	.0426	.66	.40
.589	.0317	.91		48.3	.0420	.78	.66
.760	.0314	88.02		41.2	.0414	.89	.90
.884	.0313	.06		38.3	.0412	.93	.98
1.179	.0311	.13		33.5	.0409	.99	81.04
.473	.0309	.21		30.0	.0406	92.04	.19
.572	.0308	.23		28.8	.0405	.06	.24
.768	.0307	.27		26.5	.0404	.08	.28
2.063	.0305	.34		23.0	.0401	.14	.36
.357	.0304	.38		19.0	.0398	.20	.50
.947	.0300	.53		10.0	.0392	.31	.79
3.241	.0297	.64		4.7	.0388	.39	.92
.536	.0294	.76	44	59.0	.0384	.47	82.04
4.125	.0288	.96		46.2	.0374	.66	.40
.715	.0281	89.23		31.4	.0364	.85	.80
5.304	.0273	.51		14.2	.0352	93.08	83.36
.893	.0263	.89	43	55.0	.0338	.35	.97
6.482	.0253	90.25		33.7	.0324	.62	84.44
7.072	.0242	.67		9.7	.0308	.93	85.19
.661	.0229	91.15	42	43.2	.0291	94.26	.93
8.250	.0216	.64		14.5	.0272	.59	86.74

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[49] This Bulletin, 9, p. 283, 1913.

The values for the reflecting power of silver were adopted after a consideration of the experimental data of various experimenters, especially the data of Hagen and Rubens, and of Paschen. The data are given in Table 7. Beyond 1.7μ the reflecting power of silver is practically constant and for convenience in computation the last column in Table 7 gives the correction for five reflections on the basis that beyond 2μ the reflecting power of silver is constant. A new determination of the reflecting power of silver[50] by a slight modification of the method used for measuring the diffuse reflecting power of matte surfaces gave values which are in excellent agreement with the results of other, more elaborate methods used in determining reflectivity.

TABLE 7

Showing the Reflecting Power of Silver for 3 and for 5 Mirrors

λ	R	R^3	R^5	R^5 (2 to 8μ=100%)	λ	R	R^3	R^5	R^5 (2 to 8μ=100%)
μ					μ				
0.40	0.840	0.593	0.418	0.465	0.90	0.960	0.885	0.815	0.906
.45	.880	.681	.528	.587	1.00	.964	.895	.833	.926
.48	.894	.714	....	....	1.20	.972	.918	.868	.966
.50	.900	.729	.590	.660	1.30	.974	.924	.877	.976
.55	.914	.763	....	....	1.40	.976	.928	.883	.982
.60	.925	.791	.678	.754	1.52	.977	.933	.890	.990
.65	.935	.817	....	....	1.607	.978	.935	.895	.996
.70	.942	.835	.741	.824	1.800	.9785	.937	.897	.998
.75	.947	.849	....	....	2.027	.979	.938	.899	1.000
.80	.951	.857	.774	.861	2.043	.979	.938	.899	1.000

From this it will be noticed that provided the optical system is enclosed, which preserves the silver mirrors, these corrections need be computed but once, and it is felt that they are just as reliable as (if not more reliable than) direct experimental determinations of the absorption in the apparatus which would require an additional spectroradiometric outfit. Such a direct experimental determination of the absorption in the apparatus is made daily by Mr. Abbot at the Astrophysical Observatory; but here the silver mirrors are out in the open and the measurements relate to the visible and the ultra-violet spectrum, where the optical properties of silver are entirely different from those that obtain beyond 1μ in the infra-red. By actual measurement, while engaged in the determination of the reflecting power of metals,[51] the increase in absorption of a silver mirror (which to the eye appeared slightly tarnished from standing in the air) could not be detected with certainty beyond 1.5μ when compared with an untarnished piece of this same mirror which in the meantime had been preserved in a desiccator as a standard of reference. In the ultra-violet, of course, this tarnishing would have caused a very appreciable absorption. As already stated, the spectrometer mirrors being entirely enclosed did not become tarnished[52] at least not during the few months during which a series of observations were in progress. Moreover, the application of this correction decreases the final numerical values by only about 5 parts in 1000. The correction may be even less than this amount, for this estimate was obtained by recomputation of some of the older observations in which these correction factors had not been used. It was then found, on recomputing the observations obtained at low temperatures and on redrawing the curves (from which the constants are eventually obtained) that the ordinary errors of observation were sufficient to mask the effect of the correction. The writer can not, therefore, consider as well taken any criticism that may be raised in regard to the elimination of this possible source of error, for there are too many other errors of far greater magnitude.

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[50] This Bulletin, 9, p. 283, 1913.

11. **Methods of Reduction of Data to Normal Spectrum.**—As already mentioned, the spectrometer settings—i. e., the calibration of spectrum—is obtained by computing the minimum deviation settings from the angle of the prism and the refractive indices given in Table 5. These settings are usually, of course, uneven numbers so that it is better to adopt an even number (say, 10° 0′ 0″) on the spectrometer circle. For example the minimum deviation setting for the sodium lines is 31° 36′ 31″. The minimum deviation setting for $\lambda = 1.7680\mu$ is 30° 52′ 53″. The difference is 0° 43′ 38″, and since the prism table must be rotated through one-half the required angle, the bolometer strip will be at $\lambda = 1.7680\mu$ when the prism table is rotated 0° 21′ 39″ from the zero position (the

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[51] This Bulletin, 7, p. 197; 1911.

[52] See "Note II, Preservation of silver mirrors," this Bulletin, 7, p. 221; 1910.

sodium lines at 10° 0′ 0″). Of course, in practice the spectrometer settings were made on the exact divisions of the spectrometer circle, the corresponding wave lengths being read from the calibration curve, and the values tabulated, Table 8. For example, with the sodium lines on the bolometer and the spectrometer circle reading 10° 0′ 0″ a rotation of 1° 0′ 0″ (spectrometer reading 9° 0′ 0″) placed the bolometer strip at $\lambda = 4.0307\mu$ in the spectrum.

The calibration curve was plotted to a large scale to insure accuracy. The scale adopted was 1 cm. = 30″ = 0.02μ or 1 mm. = 3″ = 0.002μ. The cross-section paper used was printed from an extremely accurate lithographic plate, 75 by 75 cm. area. This large plate made it possible to plot from 8 to 12 points in one continuous line thus increasing the accuracy. Owing to the uncertainty in the values of the refractive indices (by Paschen, Rubens, Carvallo, Langley) available when the radiation work was first begun, this calibration curve has been computed at least five times during the past seven years. The greatest uncertainty lies in the region of 1.7μ where the dispersion of flourite has a point of inflection. This is manifested in the "slit width" correction which reduces the prismatic to the normal spectrum. The method of obtaining this correction will now be described, and it is shown in Fig. 6. From the calibration curve, the wave lengths, corresponding to every minute on the spectrometer circle, were tabulated. The bolometer was constructed to subtend 4′ (width = 0.6 mm) and from the tabulated data just mentioned it was possible to determine the wave lengths comprised in 4′ of arc, in different parts of the spectrum. These values of $d\lambda$ were then plotted as ordinates against the wave lengths to which they correspond in the spectrum, as shown in Fig. 6. The earlier computations gave a wavy series of points which fall regularly above and below the smooth curve. This is no doubt due to systematic errors in the older values of the refractive indices. The final values computed from the refractive indices given in Table 5 fall close to the curve. However, in the region of 1.7μ, where there is a point of inflection, it was necessary to adjust the values to a smooth curve. The uncertainty in the values of $d\lambda/d\theta$ in this region of the spectrum fall in the fourth decimal place and while the variations appear large, it is to be

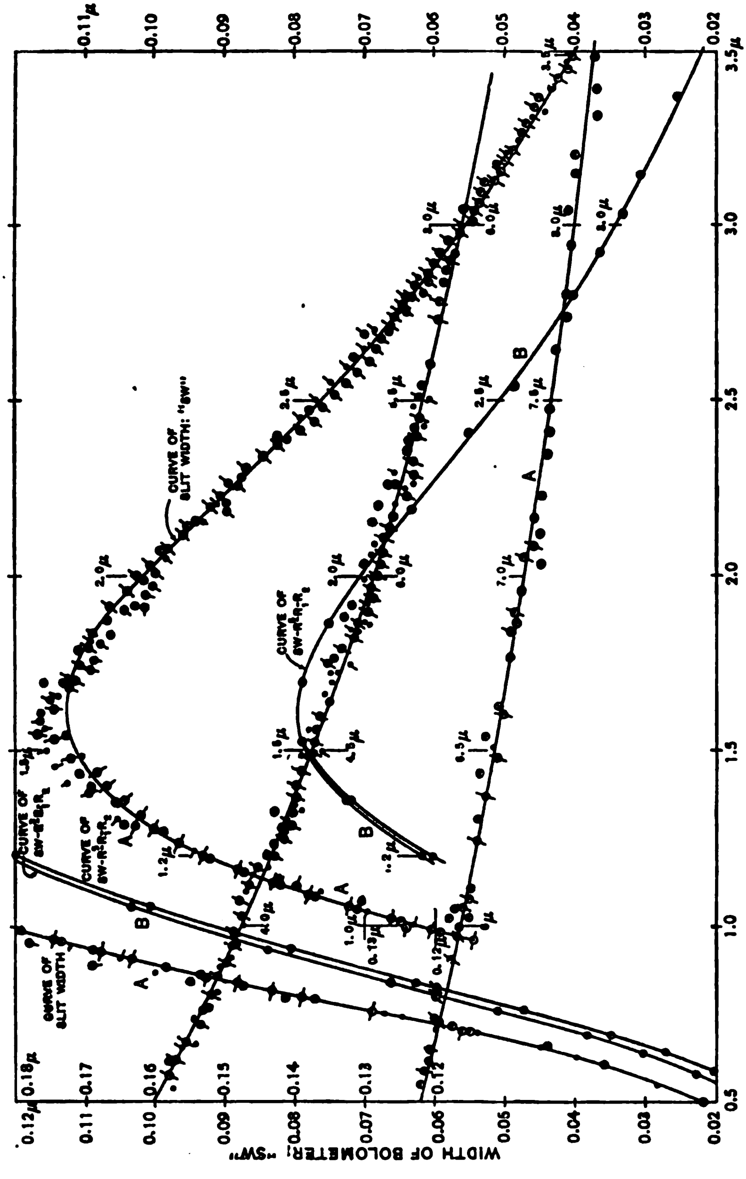

Fig. 6.—*A. Showing the width of the bolometer in different parts of the spectrum*

B. Complete correction curve for reducing data from prismatic to normal spectrum, when using 3 or 5 silver mirrors, and 4 fluorite reflecting surfaces. See Table VIII noticed that in comparison with the whole range of the spectrum they are quite small. This "slit width" curve is an excellent check upon the accuracy of the calibration curve.

The values of the "slit widths" *SW* (read from the original curve, of which Fig. 6 broken into several parts is a copy) of the bolometer for reducing from the prismatic to the normal spectrum are given in column 3 of Table 8. Columns 4 and 5 of Table 8 give the complete factors for reducing the present observations to the normal spectrum. They include the corrections for selective reflection at the prism faces, fluorite window, mirrors, etc., as given in Tables 6 and 7.

In practice the spectral energy curves were observed at every 2′ on the spectrometer circle which corresponds (by the Wadsworth minimum deviation system) to 4′, the width of the bolometer strip. From these observations the second term factor $(-\frac{1}{6}f(\alpha))$ which is necessary for reducing to a "pure spectrum" could be determined directly, the complete formula[53] for reduction to a pure spectrum being:

$$\begin{cases} D'_0 = D_{0'} - \frac{1}{6}\left(\dfrac{D_{-2'} + D_{+2'}}{2} - D_{0'}\right) + \dots \\ D_n = D'_{0'} \div sw. \end{cases}$$

In this equation $D_{0'}$ is the observed galvanometer deflection at any spectrometer setting, o'; $D_{-2'}$ is the observed deflection at a point $-2'$ preceding this setting; and $D_{+2'}$ is the deflection at a setting $+2'$ in advance; and $D'_{0'}$ is the true reading for a "pure spectrum." In order to reduce these values to the normal spectrum, D_n, the values of $D_{0'}$ are then divided by the "slit width" (s. w.) correction factors given in Table 8 using column 6 when five mirrors were employed in the spectrometer system. These values of D_n (reduced to the normal spectrum) were then plotted upon accurately made cross-section paper (1 cm = 0.2μ) and a smooth curve, from which were read certain wave lengths (as will be explained presently) for computing the position, λ_m, of the maximum emission, E_m, of the curve. From this it will be seen that the determinations of the radiation constants involve graphical as well as mathematical computations.

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[53] Runge: Zs. für Math. u. Phys., **42**, p. 205; 1897. Paschen: Ann. der Phys. (3) **60**, p. 714; 1897.

TABLE 8

Spectrometer settings		Wave lengths in μ=0.001 mm	Width of bolometer (0.6 mm=4′) in wave lengths; the "slit-width, s w."	Complete slit width correction; prismatic to normal spectrum, 3 mirrors	Complete slit width correction; prismatic to normal spectrum, 5 mirrors
°	′				
	12	0.4491	....	....	....
	10	.4660	0.0173	....	....
	8	.4855	.0195	....	....
	6	.5058	.0216	....	....
	5	.5171	.0228	....	....
	4	.5298	.0248	....	....
	2	.5579	.0283	....	....
10	0	.5893	.0338	0.0229	0.0203
	58	.6250	.0395	.0275	.0245
	57	.6462	.0430	.0303	.0271
	55	.6975	.0530	.0390	.0351
	53	.7567	.0690	.0510	.0470
	52	.7940	.0788	.0585	.0545
	51	.8355	.0880	.0664	.0626
	50	.8820	.0983	.0747	.0710
	49	.9338	.1088	.0836	.0804
	48	.9908	.1203	.0935	.0903
	47	1.0541	.1322	.1033	.1007
	46	1.1230	.1430	.1129	.1107
	45	1.1971	.1530	.1215	.1198
	44	1.2760	.1603	.1280	.1267
	43	1.3571	.1650	.1328	.1317
	42	1.4410	.1692	.1365	.1358
	41	1.5262	.1721	.1390	.1386
9	40	1.6132	.1718	.1397	.1395
	39	1.6980	.1714	.1390	.1388
	38	1.7835	.1700	.1372	.1372
	37	1.8685	.1660	.1354	.1354
	36	1.9518	.1630	.1328	Values are the same as for a 3-mirror system
	35	2.0330	.1590	.1300	
	34	2.1128	.1555	.1288	
	33	2.1895	.1515	.1235	
	32	2.2654	.1480	.1204	
	31	2.3385	.1444	.1182	
9	30	2.4098	.1414	.1149	
	29	2.4791	.1368	.1117	
	28	2.5458	.1332	.1090	
	27	2.6120	.1302	.1068	
	26	2.6757	.1275	.1043	
	25	2.7392	.1253	.1024	
	24	2.8010	.1227	.1003	
	23	2.8618	.1203	.0985	
	22	2.9213	.1183	.0966	
9	20	3.0373	.1140	.0932	
	18	3.1501	.1109	.0907	

TABLE 8—Continued

Spectrometer settings	Wave lengths in μ=0.001 mm	Width of bolometer (0.6 mm=4′) in wave lengths; the "slit-width, s w."	Complete slit width correction; prismatic to normal spectrum, 3 mirrors	Complete slit width correction; prismatic to normal spectrum, 5 mirrors
16	3.2600	0.1075	0.0878	Values are the same as for a 3-mirror system
15	3.3132	.1060	.0865	
14	3.3670	.1045	.0852	
12	3.4700	.1007	.0828	
10	3.5690	.0980	.0806	
8	3.6665	.0954	.0787	
6	3.7600	.0930	.0766	
4	3.8520	.0912	.0750	
3	3.8970	.0903	.0743	
2	3.9423	.0893	.0735	
9 00	4.0307	.0873	.0718	
55	4.2438	.0825	.0681	
50	4.4455	.0785	.0649	
45	4.6385	.0750	.0621	
40	4.8272	.0716	.0594	
35	5.0010	.0687	.0571	
8 30	5.1685	.0668	.0552	
25	5.3290	.0641	.0534	
20	5.4855	.0623	.0520	
15	5.6410	.0604	.0505	
10	5.7900	.0588	.0492	
5	5.9380	.0573	.0481	
8 0	6.0770	.0556	.0469	
7 55	6.213	.0544	.0457	
54	6.240	.0542	.0456	
50	6.348	.0530	.0447	
45	6.4775	.0520	.0439	
40	6.6055	.0505	.0429	
35	6.7200	.0495	.0420	
7 30	6.853	.0487	.0413	
20	7.090	.0468	.0401	
10	7.326	.0450	.0387	
7 00	7.546	.0433	.0878	
50	7.760	.0420	.0375	
40	7.966	.0407	....	
6 30	8.170	.0395	....	
20	8.363	.0375	....	
10	8.550	.0360	....	
6 00	8.737	....	....	
50	8.918	....	....	
40	9.09	....	....	
5 30	9.2670	....	....	

From the factors given in Table 8 it may be noticed that the reduced values of the observations, in the short wave lengths, are suppressed and that the values in the long wave lengths are greatly magnified in comparison with the original observations. This decreases the accuracy of the value of λ_m when computed from values of λ_1 and λ_2 situated far apart. Fortunately this is the region of the spectrum where errors in λ_2 have but little effect upon the computation of λ_m. For values of λ_1 and λ_2 near together the corrections for selective reflection, "slit width," etc., are closely of the same value, so that the errors introduced are much reduced. Unfortunately the presence of atmospheric absorption bands prevented extensive computations at the top of the energy curve, where λ_1 and λ_2 are close together and where the various factors are of the same magnitude on both sides of the energy curve. After eliminating atmospheric absorption, the method of obtaining the constant, C, by taking the values of λ_1 and λ_2 close together on an isothermal energy curve should not be much inferior to the method of isochromatics, owing to the small difference in the correction factors on the two sides of the maximum.

12. **Computation of λ_{max}.**—The computation of the location of the maximum emission is made from two wave lengths, λ_1 and λ_2, which have the same emissivity, $E_{\lambda_1} = E_{\lambda_2}$ on the spectral energy curve, using the formula equation (6) given on a preceding page. No computations were made in regions of the spectrum where λ_1 or λ_2 coincided with atmospheric absorption bands. In some respects this is a wasteful procedure, since the region of 2.5 to 3.2 μ, 4.1 to 4.3 μ, and 5.8 to 6.2 μ can not be utilized. However, for the series of 1911, which was determined when the humidity was exceptionally low, the water vapor has but little effect in the region of 2.9 to 3.0 μ. In addition to the absorption bands, the energy curves may be defective in other regions of the spectrum. However, there usually was no difficulty in obtaining from 8 to 10 values of λ_1 (and λ_2), which were widely separated on the energy curve. As already mentioned, the computation is partly graphical and for this purpose the energy curve was plotted upon an accurately ruled plate having an area of 40 by 50 cm, ruled in millimeters.

The computation of λ_m from values of λ_2 falling in the region of 5.9 to 6.1 μ, always gave low values, which was assumed to be due to atmospheric absorption bands of water.[54] The computation of λ_m for λ_2 falling in the region of 6.0 μ was therefore not used in making up the mean value of λ_m.

Attention has already been called to the fact that when using the first term of equation (6) for computing λ_m the values show a uniform variation. This is well illustrated in Fig. 7, A, which is obtained from a theoretical (Planck) curve. Fig. 7, B are typical experimental curves. The line slanting to the horizontal axis shows the computation when using the first term of equation (6), which is the same as equation (1), with the additional factor α/α'. This shows that the Wien equation is not applicable. The horizontal line through the mean value, resulting from computing λ_m by using all of equation (6) aids in illustrating the departure of the individual values from the mean value of λ_m. The abscissas

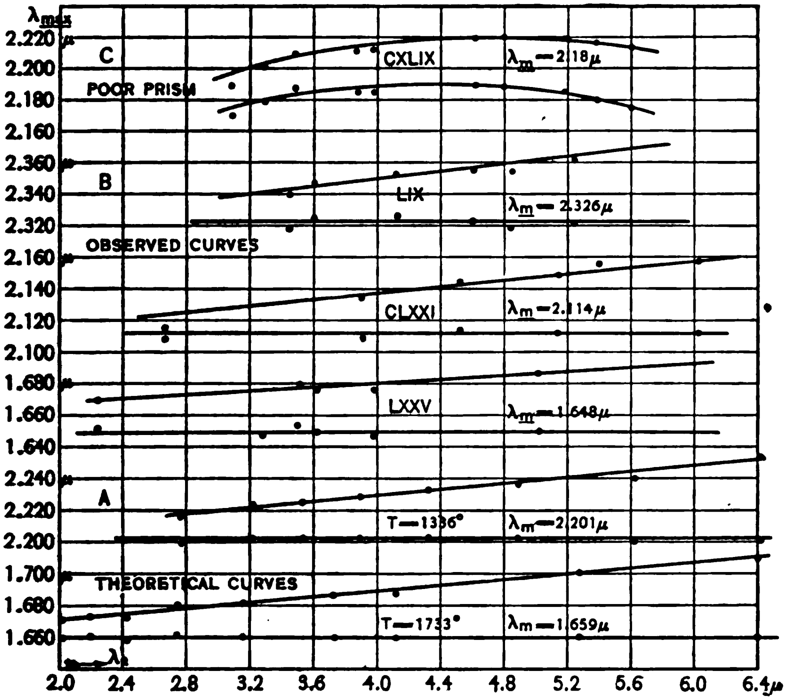

Fig. 7

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[54] This Bulletin, 7, p. 619; 1911.

are the location of the values of λ_2. Of course, instead of λ_2 the corresponding values of λ_1 might have been plotted. It may be noticed that the wide departures from the mean usually occurs when λ_2 falls in a region of atmospheric absorption at 3 μ. Energy curve No. LXXV is of interest because it gives uniform values of λ_m, but a high value of A, which seems to indicate an error in the temperature.

The curve of λ_m, Fig. 7, C, was obtained with the large fluorite prism, as already described. It fits neither the Planck nor the Wien curve, owing to an elevation at 3.5 to 4.5 μ in the energy curve. As will be noticed presently, 75 to 80 per cent of the observed energy curves fit the Planck curve, as interpreted from the closeness with which the individual computations fall to the horizontal line representing the mean value; the tolerance being $\pm 0.015\ \mu$ for curves having the maximum emission in the region up to 2.5 μ and $\pm 0.02\ \mu$ for λ_m lying in the region of 3 μ.

18. **Accuracy Attainable.**—It is a difficult matter to give an estimate of the accuracy attainable in the final results owing to the many variable factors connected with the problem. The temperature measurements are no doubt accurate to 1 part in 1500, which is entirely beyond the range of accuracy attainable in radiation measurements at the present day.

In radiation measurements at any one spectrometer setting, an accuracy of 1 part in 200 to 400 could easily be attained. But using different radiators operated at the same temperature (to 1°), as was usually done, or operating the same radiator at the same temperature on different days did not, as a usual thing, produce energy curves which were in agreement to better than 1 per cent throughout the whole spectrum. This is, of course, owing to changes in sensitivity of the radiometer, to variation in humidity, etc. It is a severe test that has heretofore never been undertaken.

The computation of the constants involves some uncertainties, but owing to the large-sized and accurately ruled cross-section paper used this is of minor importance. The scale to which the energy curves were plotted was 1 mm $= 0.02\mu$, and it was an easy matter to read the values of λ_1 and λ_2 to 0.005 μ. Frequently when the curves were poor the values were read to 0.01 μ. It was the common experience to find that for values of λ_1 and λ_2, ranging over the whole curve, the individual values of λ_m differed by 0.005 to 0.01 μ which is of the order of 1 part in 300 to 200 since the λ_m falls between 2 and 3 μ. This is owing to the fact that small variations in the value of λ_2 (which fall in the region of the spectrum where the energy is weak and difficult to observe) have but little effect in equation (6). It is for this reason that the present method seems superior to the determination of isochromatic energy curves, in spite of the fact that by the latter method the absorption in the apparatus is eliminated. By taking λ_1 and λ_2 over a wide range of the spectrum, the errors in calibration (in refraction and in the slit-width correction), in changes in sensitivity, etc., are reduced to a negligible value. This is owing to the fact that when E_1 and E_2 (for λ_1 and λ_2) are close together they fall in the doubtful region at 1.6 to 2 μ (for the temperatures investigated), where the slit-width reduction factors are known with the least accuracy; but they are of nearly the same value for $E_1 = E_2$. When λ_1 and λ_2 are far apart, quire a large error (owing to the uncertainty in the correction for reflecting power at λ_1) must occur before it becomes noticeable in computing λ_m.

There appears to be no systematic variation in the different values of the constant, C, with temperature (which might result from errors in the temperature scale and in the computation of λ_m), from which it appears that the Planck formula is sufficiently accurate for the temperature from 500° to 1500°. The best observational work could be done in the range of 800° to 1400°, the lower temperature being such as to give a sharp energy curve and the higher temperature being still within the range of knowledge of the temperature scale.

The effect of " field light " scattered over the spectrum owing to the imperfections in the prism, was tested in various ways, the assumption being made that this scattered light was uniformly distributed, which of course could hardly be true for diffuse reflection. One test for diffuse light was to set the bolometer at 0.32 μ, where the reflecting power of silver is practically zero, and measure the spectral radiation of a highly incandescent body, e. g., a Nernst glower. For the perfectly clear fluorite prism used in this work no radiation could be detected. Another test was to set the bolometer in the yellow part of the spectrum, at a point where a sample of Schott's monochromatic red glass becomes opaque, the source of radiation being a Nernst glower. The test was made on a very windy day, when a high precision was not possible, but for measurement to 1 part in 300 no scattered radiations could be detected. That the amount of diffuse light is extremely small in this prism (No. 1) is shown indirectly from the data on the transmission of water and of cupric chloride solutions (this Bulletin, **7**, p. 619, and **9**, p. 110), which are entirely opaque in the region of 1.2 to 2 μ, where one would expect stray radiation.

These tests were not made on the large fluorite prism, described elsewhere, except at 0.32 μ, where the amount of diffuse light was barely measurable. Nevertheless, to the eye there appeared to be considerable diffuse red light extending far into the infra-red. Furthermore the spectral energy curves obtained with this prism are distorted by an excess of radiation in the region of 3.5 to 4 μ, which appears to be caused by diffuse radiations superposed upon the spectrum. It will be shown presently that but very few (25 per cent) of the spectral energy curves obtained with this prism fit the Planck equation, and the constant, C, is much higher than obtains with any of the determinations with the perfectly clear prism. Perhaps this will explain a similar condition in the curves obtained by Paschen (loc. cit.) and his higher values of the radiation constants.

The accuracy attained in the final result, estimated from the probable error, is of the order of 0.2 per cent, i. e., the systematic errors are such that the mean values of the various sets of observations differ by 1 to 2 parts in 1000. This means an uncertainty of ±15 to ±30 in the value of the constant $C = 14\,450$.

V. EXPERIMENTAL DATA; SERIES OF 1909

This series of observations consists of 34 spectral energy curves obtained with an unpainted porcelain radiator, Fig. 2, which, as in the experiments of Lummer and Pringsheim, was placed directly before the spectrometer slit. The water-cooled shutter and perforated water-cooled diaphragm shown in Fig. 3 were used. The inner heating coil burned out while observing energy curve No. XIX and the radiator was rewound. For the entire research after No. XXV a small knife-edge support was placed under the inner radiator, as explained elsewhere, to prevent it from sagging.

The whole series therefore contains three distinct sets of observations. However, owing to the fact that the radiator was bent from excessive heating and owing to the uncertainty as to the entire elimination of radiation from the side walls and the diaphragms, this series is given no weight in considering the final results.

The spectroradiometric apparatus consisted of an air bolometer (No. 7, resistance of each arm 4.1 ohms) and a small perfectly clear fluorite prism (No. 1, described elsewhere). The bolometer was placed at the focus of a hemispherical mirror 5 cm in diameter. The observations were made under very great difficulties owing to unsteadiness caused by air currents. This made observing almost impossible beyond 4μ in the infra-red, where the deflections were small.

As in each succeeding series, the thermocouples, potentiometer, and standard cell were standardized before and after the series of observations. The mirrors were resilvered at the beginning of each series of observations, so that, in discussing the various series of observations made in subsequent years, no mention will be made of these facts.

In the "series of 1909" observations the radiations from the furnace covered only about one-half of the bolometer strip. In a subsequent work an image of the radiating wall was projected upon and entirely covering the spectrometer slit. In this manner only radiations from the central diaphragm could pass into the spectrometer slit and from thence pass to the bolometer strip which was entirely covered by the incident radiations.

The computations of λ_m by equation (6) give high values, which, for one particular energy curve, the preliminary data of which was published some time ago,[55] gave unusually uniform values of λ_m, for values λ_1 and λ_2 taken over the whole curve. This was one of the few curves completely worked out by the long method of equation (6). All the curves had of course been worked out by equation (1) and, as the title of the paper [55] indicated, it was found that the computations made by equation (1) (the Wien equation) failed to give a uniform value of λ_m computed by taking values of λ_1 and λ_2 over the whole spectrum. In the most recent computations, using a different dispersion (calibration) curve, and including the various correction factors mentioned on a preceding page, it is found that neither the Wien nor the Planck system of computation (equations (1) and (6)) gives uniform values of λ_m. The spectral energy curves appear to bulge upward at 3.5 to 4.5μ. Just how much of this is owing to stray light is difficult to say. As explained elsewhere the whole series is inconsistent with what has been observed since then under more favorable conditions, so that, in the final summary of the work, the numerical results are omitted. However, in view of the discordant results obtained by other experimenters, these data are of interest in showing what great variations may be obtained in the numerical results when using the same prism under various conditions. The results obtained in subsequent years are in excellent agreement. This is especially true if the "series of 1911 and 1912," in which the various sources of error appear to have been eliminated as thoroughly as seems possible with the present type of apparatus. The numerical results of the "series of 1909" are given in Table 9. The data are arranged according to the increase in temperature at which the observations were made. The first column gives the serial number of the experiment. The second column gives the form of the energy curve, "P = Planck," "W = Wien." The "WP" means that the curve lies between the Planck and the Wien equation and is closer to the latter. As explained elsewhere, the criterion for judging the form of the energy curve is the uniformity of the values of λ_m for different values of λ_1 and λ_2 as computed by equation (6) before and after the application of the second term correction factor. If the first term of equation (6) gives uniform values, without deducting the second term, then the curve evidently is of the Wien equation type. If after deducting the second term the values of λ_m are uniform, then the form of the curve is of the Planck equation type; but if, after deducting the second term, the values of λ_m pass through a maximum value (i. e., the second terms overcorrects the results), see Fig. 7, *C*, then it is assumed that the form of the experimental energy curve lies between the Planck and the Wien equations. In the column of λ_m the probable error of the result refers to the departure from the mean value obtained from the number of computations (sixth column) made on any given energy curve.

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[55] Jahrbuch Radioaktivität u. Elektronik, 7, p. 1, 1911, "A characteristic of spectral energy curves."

TABLE 9

Series 1909—Bolometer No. 7, Black Body at Slit, Water-Cooled Shutter No. 1

[Energy Curves, I-XXXV]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$c-\alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
IX	P	738	3.986	±0.001	4	2942	14 606
X	W	819	3.719	.001	5	3046	15 123
VIII	P+	963	3.233	.015	4	3113	15 458
XI	?	1020	2.984	.017	6	3044	15 112
II	WP	1147	2.671	.012	5	3064	15 211
XV	?	1192	2.560	.005	7	3052	15 151
IV	W?	1229	2.434	.013	4	2991	14 853
XIII	WP	1273	2.351	.005	6	2993	14 860
III	W?	1293	2.295	.008	4	2967	14 733
XII	WP?	1322	2.248	.006	5	2972	14 756
VI	WP	1336	2.238	.006	7	2990	14 846
I	W	1388	2.149	.014	4	2983	14 810
V	W	1420	2.085	.005	5	2961	14 700
VII	P?	1564	1.885	.009	5	2948	14 638
XIV	P+	1624	1.826	.002	7	2965	14 724
XVIII	WP	1667	1.789	.001	6	2982	14 807
XVI	W?	1702	1.756	.004	7	2989	14 839
XVII	P?	1702	1.774	.003	6	3019	14 991
Mean...	....	....	....	....	....	3001	14 901
XX	W	777	3.780	±0.004	4	2937	14 583
XXVIII	W?	1073	2.790	.011	3	2994	14 864
XXXII	W−	1192	2.495	.017	5	2974	14 766
XXIX	W?	1270	2.356	.003	6	2992	14 856
XXII	W	1322	2.242	.002	6	2964	14 716
XXXI	PW	1336	2.235	.002	6	2986	14 826
XXI	PW	1358	2.173	.002	5	2951	14 652
XXIII	PW	1420	2.082	.005	7	2956	14 679
XXIV	P?	1516	1.956	.001	5	2965	14 723
XXV	PW	1600	1.850	.004	6	2960	14 697
XXXV	W	1611	1.860	.003	6	2996	14 878
XXVII	WP	1660	1.837	.004	8	3049	15 151
XXVI	W	1667	1.751	.004	5	2919	14 493
XXX	P	1703	1.752	.001	8	2984	14 814
XXXIII	WP	1737	1.734	.001	9	3012	14 955
XXXIV	W−	1765	1.711	.005	7	3020	14 994
Mean...	....	....	....	....	....	2979	14 790

In this and in the subsequent tables the values of λ_m are tabulated to the nearest even whole number. Similarly, the values of the temperatures were read to even whole numbers from the thermocouple calibration curves; for it seemed futile to read temperatures to fractions of a degree and include the correction for reduction to the absolute scale when the temperature scale can not be guaranteed to better than 1°.

VI. EXPERIMENTAL DATA; SERIES OF 1910

In the first set of measurements (XXXVI to XL, inclusive) an air bolometer (No. 9, resistance of each strip 6.45 ohms) was used. It was covered with a glass crystallizing dish with a fluorite window for admitting the radiation upon the bolometer strip. The bolometer platinum, being much thinner than in the preceding series, was very seriously affected by air currents, which made it impossible to accurately read the galvanometer deflections.

The second set (XLI to LIV) of energy curves was obtained with a vacuum bolometer (No. 10, resistance of each strip 5.6 ohms) at the focus of a hemispherical mirror. The radiating diaphragm of a new straight porcelain tube was focused upon the spectrometer slit, as shown in Fig. 1. The water-cooled shutter, No. 1, Fig. 3, was placed at *S* in Fig. 1.

Owing to the extreme unsteadiness of the bolometer, the first set of measurements can be given but little, if any, weight in comparison with the rest of the observations. There is also some uncertainty in regard to the temperature scale, which seems to be higher than for the two subsequent years. The sensitivity of the bolometer had a tendency to increase during a series of observations. This, of course, could be adjusted in plotting the curves for computation; but it is never as satisfactory as to have the observations entirely free from changes in sensitivity. Hence, in making up the summary of the most reliable data obtained up to this time, this series is given no weight in comparison with the data obtained in 1912, which, in spite of the small systematic errors for the different sets of observations, are considered the most reliable. The various data are given in Table 10, the explanation of the various columns being the same as for Table 9 of "series of 1909."

TABLE 10

Series 1910, I.—Bolometer in Air, no Hemispherical Mirror

[Energy Curves, XXXVI–XL]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$C = \alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
XXXIX	?	1180	2.460	±0.008	5	2903	14 413
XXXVIII	W	1278	2.272	.007	4	2904	14 417
XXXVII	W	1341	2.148	.005	6	2880	14 302
XXXVI	P	1423	2.025	.002	5	2882	14 307
XL	P	1528	1.902	.001	7	2906	14 430
Mean...	....	....	....	....	....	2895	14 374

Series 1910, II.—Vacuum Bolometer, Hemispherical Mirror

[Energy Curves, XLI–LIV]

LII [a]	?	1004	2.986	±0.003	4	2918	14 486
XLVII [a]	?	1104	2.642	.010	4	2917	14 482
LI [a]	P	1178	2.472	.005	7	2912	14 458
XLVI	PW	1204	2.441	.001	9	2939	14 592
XLV	P	1280	2.290	.001	5	2931	14 554
L	PW	1305	2.247	.004	8	2932	14 559
XLIV	PW	1341	2.181	.001	8	2925	14 521
XLIII	P	1380	2.145	.001	8	2960	14 697
XLIX [a]	P	1423	2.054	.001	8	2923	14 512
XLII	P	1423	2.058	.002	6	2929	14 540
XLI	P	1480	1.991	.001	7	2947	14 631
XLVIII	P	1504	1.960	.002	9	2948	14 636
LIV	P	1530	1.914	.003	4	2928	14 540
LIII	P	1576	1.873	.002	5	2952	14 656
Mean...	....	....	....	....	....	2933	14 562

[a] Poor curves.

VII. EXPERIMENTAL DATA; SERIES OF 1911

This series (LV to LXXXIV) of spectral energy curves was obtained on an unpainted radiator of Marquardt porcelain, which has a higher melting point and is a better electrical insulator than ordinary porcelain.

The water-cooled shutter, No. 2, Fig. 3, with an opening 4.5 mm in diameter, was attached to the radiator and the whole optical system rendered more air tight, which rendered a greater reduction in humidity.

The potentiometer installation was renovated and tested for insulation. A new fluorite window was placed over the bolometer, and a new resistance was placed in the battery circuit for keeping a constant bolometer current. The bolometer was blackened a little more with soot from a sperm candle. Thin vanes of bolometer platinum were attached to the galvanometer, which completely damped the deflection on a 2.5 seconds single swing. Previously the ballistic throw of the galvanometer was observed. Improvements were also made in the method of viewing the spectrometer circle.

A set of seven isochromatics (LXXXV, 1 to 7) was obtained, which furnished material for computing the constants from spectral-energy curves by means of equation (6). However, owing to the fewness of the observations which makes it difficult to draw an accurate energy curve, this set (LXXXV, 1 to 7) is to be given no weight. The isochromatics appeared unsatisfactory, owing probably to a lack of sufficient time for the radiator to attain a uniform temperature, and the observations were never computed.

The average humidity during the time when this series of observations was obtained was lower than for the series of 1912, and for this reason it was possible to make computations of λ_m with values of λ_x falling at 3.0μ and 3.2μ, which was not possible when the humidity was much higher.

A number of the curves in this series have the property of being slightly higher than required by the Planck equation (for the region beyond 4.8μ), so that the second term factor in equation (6) does not reduce the values of λ_m to a uniform value which is independent of the location of λ_x. The mean value of λ_m is therefore slightly higher than usually obtained. This makes but little difference in the final results; but it is of interest to record the fact, which goes to show how variable are the results obtained with the same apparatus and fluorite prism, in spite of all the precautions taken to eliminate all possible errors. The writer is therefore inclined to believe that some of the discrepancies observed

TABLE 11

Series 1911—Water Cooled Shutter No. 2, Attached to Black Body

[Energy Curves, LV-LXXXIV]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$C=\alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
LXX [a]	PW	739	3.918	±0.005	3	2895	14 376
LXXI [a]	?	776	3.756	.019	4	2914	14 470
LXXII [a]	?	826	3.530	.009	3	2916	14 478
LXIX	P	865?	3.388	.002	4	2931	14 551
LXVI [a]	PW	1007	2.900	.008	4	2920	14 498
LXVII [a]	PW	1050	2.782	.004	4	2920	14 497
LXVIII [a]	P	1051	2.778	.005	5	2918	14 487
LXI	PW	1150	2.540	.001	5	2921	14 502
LX	P	1201	2.423	.002	6	2909	14 448
LIX	P	1249	2.326	.002	8	2906	14 427
LVI	P	1277	2.274	.002	6	2904	14 418
LVIII	P	1338	2.176	.002	6	2911	14 454
LXV	P	1350	2.150	.001	6	2903	14 412
LXXXIV	PW	1375	2.137	.005	6	2938?	14 589?
LVII	PW	1401	2.080	.002	3	2913	14 466
LV	P	1419	2.057	.002	8	2918	14 490
LXXXIII	P	1474	1.981	.002	7	2920	14 497
LXIV	P	1474	1.978	.001	5	2916	14 478
LXIII	P	1499	1.939	.003	6	2907	14 430
LXII	P	1524	1.910	.003	7	2910	14 445
LXXXII [b]	P	1548	1.898	.004	6	2938?	14 588?
LXXXI	P	1595	1.831	.003	4	2921	14 503
LXXIV	P	1597	1.825	.003	6	2915	14 472
LXXX	P	1620	1.798	.002	4	2912	14 466
LXXIX	P	1648	1.775	.002	4	2923	14 513
LXXVIII [a]	P	1673	1.752	.002	4	2931	14 553
LXXIII	P	1700	1.712	.002	5	2911	14 449
LXXVII [a]	P	1720?	1.721	.007	4	2961?	14 703?
LXXVI [b]	P	1773	1.649	.002	4	2921	14 502
LXXV [b]	PW	1796	1.648	.005	10	2960?	14 696?
Mean...	....	....	....	....	....	2914	14 469 (14 495)
LXXXV (1) [a]	P	969	3.000	0.003	6	2907	14 434
(2)	?	1139	2.566	.003	3	2923	14 511
(3)	P	1316	2.240	.004	4	2948	14 636
(4)	P	1448	2.020	.002	5	2925	14 523
(5)	P	1564	1.885	.005	4	2948	14 638
(6)	P	1690	1.740	.003	3	2941	14 600
(7)	P	1758	1.673	.001	5	2941	14 603
Mean...	....	....	....	....	....	2933	14 563

[a] Poor curves.

[b] Bolometer sensitivity varied.

by other experimenters when modifying their apparatus may be due to these systematic errors and not due entirely to the different prisms used.

The data for the "series of 1911" are given in Table 11, the arrangement of this table being the same as for the "series of 1909" given on a preceding page. The results of this series are in excellent agreement with the subsequent data (series of 1912), which was obtained with entirely new adjustments. Considerable confidence is therefore placed in these two series of observations. The mean value of all the energy curves gives $C = 14\ 495$. If we exclude the four energy curves indicated (?) in Table 11, for which the values of C are extraordinarily high, the mean value is but slightly reduced, being $C = 14\ 469$. The writer feels justified in omitting these four high values because in at least two cases (LXXV and LXXXII) the bolometer was freshly exhausted and the residual gases were changing from hydrogen (and nitrogen) to the characteristic carbon dioxide spectrum. The radiation sensitivity, therefore, probably changed more than indicated by direct experiment. For, as already explained, the radiation sensitivity of the bolometer tended to decrease and the galvanometer sensitivity tended to increase, so that after such a prolonged series of observations these variations may have escaped notice.

VIII. EXPERIMENTAL DATA; SERIES OF 1912

1. **White Radiating Walls; Prism No. 1.**—After readjusting the apparatus throughout, a series of observations (LXXXVI to XCII) was made upon the unblackened Marquardt tube used the preceding year, to obtain a check upon the previous work and also upon the work that was to follow. The fluorite prism, No. 1, was reset, and minor changes were made in the entire apparatus. Unless otherwise stated, the water-cooled shutter No. 2 was used throughout this series. The data are given in Table 12, the mean value being $C = 14\ 463$.

TABLE 12

Series 1912, I—White Radiating Walls, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy Curves, LXXXVI–XCII]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$C = \alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
XCII [a]	?	1122	2.605	±0.005	3	2922	14 508
LXXXVIII	P	1209	2.408	.003	6	2910	14 451
XCI [a]	P	1223	2.374	.002	4	2904	14 418
LXXXVII	PW	1242	2.345	.001	5	2912	14 459
LXXXVI	P	1350	2.154	.002	6	2908	14 438
LXXXIX [b]	P	1419	2.056	.003	7	2916	14 480
XC [a]	PW	1427	2.045	.006	5	2918	14 486
Mean...	....	....	....	....	....	2913	14 463

[a] Furnace heated by outer coil only.

[b] Poor curve.

2. **Black Radiating Walls.**—For this set of observations (XCIII to CVI) the inner porcelain tube was painted with a thick coat of chromium oxide. Owing to the smallness of the opening, the inner tube, *A*, Fig. 4, had to be removed and the painting done in strong sunlight. The pigment was mixed with water and applied with a fine-haired brush. The front thermocouple rested in contact with the chromium oxide. At the end of the series no effect of the oxide upon the thermocouple could be observed. The humidity was lower than usual for this series. The water-cooled shutter No. 2 was used. The temperature of the water, just after leaving the perforated diaphragm, was 9.4° when the radiator was at a temperature of 1100°. Since the thin metal door, which permitted the passage of radiations from the furnace to the spectrometer, was directly in contact with the water-cooled diaphragm, it was assumed that (as on previous tests) the temperature of the door was not much above that of the flowing water. This question is discussed elsewhere. The data of this series are given in Table 13, the mean value being $C = 14\ 432$.

TABLE 13

Series 1912, II—Black (Cr_2O_3) Radiating Walls, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy Curves, XCIII–CVI]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	C= $\alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
CVI[a]	P	1025	2.824	±0.001	5	2895	14 372
XCIX	P	1153	2.507	.002	4	2891	14 356
XCVIII[a]	P	1223	2.375	.004	4	2904	14 419
XCVII	P	1301	2.226	.002	6	2896	14 379
CV	P	1338	2.183	.002	5	2921	14 503
XCV[a]	P	1351	2.145	.001	4	2898	14 388
XCVI	P	1377	2.104	.003	4	2897	14 385
CIV	P	1401	2.080	.003	6	2914	14 470
XCIV	P	1420	2.050	.004	7	2909	14 442
CII	P	1453	2.003	.008	7	2910	14 450
CIII	P	1479	1.973	.004	5	2918	14 491
XCIII	P	1501	1.944	.004	4	2917	14 485
CI	PW	1525	1.908	.005	5	2910	14 447
C	P	1687	1.726	.002	5	2912	14 457
Mean...	....	....	....	....	....	2907	14 432

[a] Poor curves.

3. **New Radiator; White Walls.**—This set of energy curves (CVII to CXIII) was obtained with a new unpainted Marquardt porcelain tube. The platinum ribbon was 20 mm wide at the center and decreased uniformly to 11 mm in width at the ends, which is somewhat narrower than for the preceding radiator. The end diaphragm was broken away, as shown in Fig. 4, *B*, so as to permit of painting the inner walls without removing the tube. The end was, of course, closed with a similar porcelain diaphragm when ready for observations. The thermocouple was entirely inclosed in a small unpainted porcelain tube, as shown in Fig. 4, *B*. The axial adjustment of the radiator was made anew; and the optical path was traced and adjusted throughout the whole apparatus by the light coming from the radiator heated to 1300°. The water-cooled shutter No. 2 and fluorite prism No. 1 were used.

The data of this series are given in Table 14, the mean value being $C = 14\ 466$.

TABLE 14

Series 1912, III—New Radiator, White Walls, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy Curves, CVII–CXIII]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$C = \alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
CXIII[a]	?	1151	2.540	±0.002	3	2921	14 504
CX	PW	1223	2.383	.003	6	2914	14 460
CXII	P	1276	2.275	.001	6	2903	14 412
CIX	P?	1352	2.155	.002	7	2914	14 466
CXI	P	1379	2.109	.004	5	2911	14 451
CVIII	P	1453	2.003	.003	5	2910	14 450
CVII	P	1527	1.913	.003	4	2921	14 508
Mean...	....	....	....	....	....	2913	14 466

[a] Poor curve.

4. **New Radiator; Black Walls.**—For this set of energy curves (CXIV to CXXIII) all the adjustments and accessory apparatus were the same as for the preceding series. The inner walls, the front side of the radiating diaphragm, and the short tube covering the thermocouple were painted with a layer of chromium oxide. On this layer was painted a thick coat of cobalt oxide. It was found that the inclosed thermocouple responds almost as quickly to temperature changes as obtained in the bare thermocouple. At the completion of the set it was found that some of the oxide had become detached from the short porcelain tube covering the thermocouple, which left this tube a bluish white. In spite of this fact, however, the percentage of curves fitting the Planck equation is noticeably larger for the blackened than for the unblackened tubes.

The data of this series are given in Table 15, the mean value being $C = 14\ 459$, or if we exclude the last value, which is extraordinarily high (a poor curve), the mean value is practically unchanged, being $C = 14\ 446$.

TABLE 15

Series 1912, IV—New Radiator, Black ($Cr_2O_3 + 2Co_2O_3$) Walls, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy Curves, CXIV–CXXIII]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$C-\alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
CXXIII[a]	P?	876	3.312	±0.004	3	2901	14 405
CXXII	P	1025	2.826	.002	8	2897	14 382
CXXI	P	1077	2.704	.005	5	2912	14 459
CXVIII	P	1154	2.516	.003	6	2903	14 414
CXX	PW	1223	2.376	.001	5	2906	14 428
CXVII	P	1276	2.280	.001	5	2909	14 445
CXIX	P	1353	2.156	.002	6	2917	14 486
CXVI[a]	P	1377	2.122	.007	6	2922	14 507
CXV	P	1454	2.007	.005	6	2918	14 488
CXIV[a]	P	1503?	1.954	.004	4	2936	14 580?
Mean. . .	. . . .	. . . .	. . . .	. . . .	. . . .	2910	14 446 (14 459)

[a] Poor curves.

5. **Blackened Radiator; New Adjustments.**—In this series (CXXIV to CXL) the short porcelain tube inclosing the thermocouple was covered with iron oxide (from writing ink, which was then burned into the tube by means of a blast lamp) over which was painted a layer of chromium oxide. To do this, the water-cooled shutter had to be removed. This series therefore differs from the preceding only in that the radiator was repainted with a mixture of chromium and cobalt oxides and the complete optical system was readjusted. At the highest temperatures (1300° to 1500°, series CXXXVIII to CXL) the radiator was heated by electric current from a motor-generator operated on a storage battery. For temperatures up to 1250° there was little or no conduction of current from the heating coils to the thermocouples.

The data of this series are given in Table 16, the mean value being $C = 14\,501$. If we exclude the three (indicated in Table 16) which have either a high probable error for the λ_m, which are poor curves or were obtained at such high temperatures that the use of a fluorite prism is questioned, the value is $C = 14\,476$.

TABLE 16

Series 1912, V—Blackened Radiator, New Adjustments, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy Curves, CXXIV–CXL]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$C = \alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
CXXXV [a]	?	1026	2.831	±0.005	5	2905	14 423
CXXXII [a]	P	1077	2.703	.004	5	2911	14 455
CXXXIV	PW	1153	2.520	.003	6	2905	14 425
CXXXI	P	1194	2.441	.003	4	2914	14 469
CXXIX	P	1224	2.380	.001	6	2913	14 464
CXXVI	P+	1276	2.284	.006	9	2914	14 469
CXXXIII	P+	1302	2.237	.002	6	2913	14 461
CXXXVII	PW	1302	2.242	.003	7	2920	14 498
CXXX	P	1338	2.182	.003	5	2920	14 497
CXXVIII	P+	1352	2.160	.004	4	2921	14 501
CXXV	P	1378	2.118	.004	5	2918	14 483
CXXXVI	P	1421?	2.068	.003	5	2939	14 588?
CXXVII	P+	1454	2.008	.004	9	2920	14 497
CXXIV	P+	1503	1.961?	.007	4	2948	14 629?
CXL [b]	P	1627	1.798	.003	5	2925	14 524
CXXXVIII [b]	PW	1663	1.756	.004	5	2921	14 500
CXXXIX [a,b]	P+	1796	1.639	.002	8	2945	14 631?
Mean...	....	....	....	....	....	2915	14 476 (14 501)

[a] Poor curves.

[b] Alternating current used for furnace heating coils.

6. **Blackened Radiator; Prism No. 2.**—In this set of observations (CXLI to CXLVII) all the adjustments were the same as in the preceding series. The small fluorite prism was replaced by a large one, No. 2, described elsewhere. This was for the purpose of testing the effect of the prism, all other adjustments remaining the same. The humidity was lower than for the preceding series, so that the distortion of the energy curves in the region of 3.5 to 4μ is not due to atmospheric absorption beyond 5μ, but is no doubt

owing to defects in the structure of the prism, which visually caused much more stray light than in a clear prism. The spectral energy curves obtained with this prism are entirely different from those obtained with a clear prism. As shown in Table 17, only about 30 per cent of the energy curves fall within the limits set for agreement with the Planck equation.

TABLE 17

Series 1912, VI—Blackened Radiator, Fluorite Prism No. 2, Water-Cooled Shutter No. 2

[Energy Curves, CXLI–CXLVII]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$c = \alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
CXLII[a]	W	1077	2.745	±0.007	4	2956	14 679
CXLVII	PW	1154	2.580	.001	9	2977	14 783
CXLVI	W	1194	2.475	.002	9	2955	14 673
CXLI	P	1225	2.402	.004	7	2942	14 610
CXLV	P	1277	2.331	.003	9	2977	14 780
CXLIV	P?	1352	2.188	.001	10	2958	14 688
CXLIII	P	1454	2.055	.001	8	2988	14 836
Mean...	....	....	....	....	....	2969	14 721

[a] Poor curve.

7. **New Thermocouple; Prism No. 2.**—The object of this series (CXLVIII to CLV) was to test the effect of a change in thermocouples, the large fluorite prism, No. 2, and the other accessories remaining unchanged. The thermocouple was entirely new, and unused except for obtaining its calibration. The thermoelement at the rear of the radiating diaphragm was recalibrated. The coating of cobalt oxide, which was on the short porcelain tube inclosing the thermoelement, was rendered more adhesive by mixing the pigment with a small quantity of kaolin. This was burned upon the tube before mounting the thermocouple in the radiator, which was then repainted before resetting the water-cooled shutter.

As in the preceding series, only a small proportion of the energy curves fit the Planck equation. The data of this series are given in Table 18.

TABLE 18

Series 1912, VII—Blackened Radiator, New Thermocouple, Fluorite Prism No. 2, Water-Cooled Shutter No. 2

[Energy Curves, CXLVIII–CLV]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$c = \alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
CLII[a]	W	1078	2.727	±0.003	3	2940	14 596
CLV	WP	1195	2.467	.006	5	2948	14 638
CLI	WP	1223	2.403	.003	10	2939	14 592
CL	PW	1277	2.301	.002	10	2938	14 589
CLIV	P	1301	2.271	.001	8	2955	14 670
CXLIX	PW	1353	2.180	.001	10	2950	14 645
CLIII	WP	1377	2.145	.003	9	2954	14 665
CXLVIII	P	1453	2.035	.002	7	2957	14 681
Mean						2947	14 634

[a] Poor curve.

8. **New Thermocouple; Prism No. 1.**—This set (CLVI to CLXVII) of energy curves was obtained with the small fluorite prism, No. 1, to test the effect of a small displacement, 58′, of its center of rotation upon the prism table. This is not a very important factor, but it seemed worth while to test it. The rest of the apparatus, including the thermocouple, was the same as in the preceding experiment. The optical path was, of course, tested as usual for adjustment upon the spectrometer slit, upon the prism face, and upon the bolometer. The result of this test show that within the usual experimental errors of observation and variation in humidity there is no deviation in the values of the constants which can be attributed to a displacement of the axis of rotation of the prism mirror system.

This and the following series of observations were made under more unfavorable conditions than usually encountered. Curve CLXII was poor owing to unsteadiness of the bolometer, caused by a low vacuum; and the last day's work (CLXV to CLXVII) was spoiled by tremors which at times made it impossible to read the galvanometer. While observing a spectral energy curve the platinum ribbon on the inner radiator became disrupted, so that curves CLXVI and CLXVII were obtained by heating the inner tube, Fig. 2, by radiation from the outer heater. No difference is to be observed in its effect upon numerical results as compared with curve CLXV, which was obtained on the same day. There was, of course, a greater lag in controlling the temperature when heating the inner tube by radiation than when heating it by means of the platinum ribbon with which it was surrounded.

The data of this series are given in Table 19, the mean value being $C = 14\ 518$, or if we exclude the last three in the series, which evidently can not be given equal weight with the rest, the mean value is $C = 14\ 461$.

TABLE 19

Series 1912, VIII—Blackened Radiator, New Thermocouple, Fluorite Prism No. 1, Water-cooled Shutter No. 2

[Energy Curves, CLVI–CLXVII]

No.	Form of energy curve	Absolute tem-perature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$C-\alpha\lambda_{max}T$
			Mean value	Probable error	Number of com-putations		
		°	μ	μ			
CLIX[a]	?	806	3.610	....	....	2910	14 447
CLX	WP	879	3.300	±0.003	2	2901	14 402
CLXI[b]	P	953	3.052	.003	2	2909	14 441
CLVIII	P	1077	2.703	.002	7	2911	14 454
CLVII[c]	P?	1223	2.380	.004	6	2911	14 453
CLVI	P	1277	2.286	.003	7	2920	14 497
CLXIV[d]	P	1300	2.248	.004	8	2923	14 513
CLXVII[e,b]	WP	1314	2.236	.003	7	2938?	14 588?
CLXIII	P	1376	2.120	.004	6	2917	14 482
CLXVI[b,d]	P	1377	2.140	.002	5	2947?	14 634?
CLXII[f]	P+	1452	2.030	.004	10	2948?	14 639?
CLXV[d,b]	P+	1539	1.920	.003	9	2955?	14 671?
Mean...	....	....	....	....	....	2912	14 461 (14 518)

[a] Very poor curve, λ max by inspection.

[b] Poor series, tremors.

[c] Poor curve.

[d] Radiation sensitivity changed.

[e] Furnace heated by outer coil only.

[f] Bolometer unsteady; low vacuum.

9. **Water-Cooled Shutter No. 1; Prism No. 1.**—In this set (CLXVIII to CLXXV) the water-cooled shutter, No. 1, and the separate water-cooled diaphragm, Fig. 3, with an opening 6.7 mm. (placed at *S*, Fig. 1) was used with the object of testing the effect of the size of the opening in the water-cooled diaphragm, upon the energy curves. It was not possible to prevent, so effectively as with shutter No. 2, the entrance of air into the spectrometer boxes. The humidity was higher than in any of the preceding sets of observations, the sensitivity of the galvanometer was continually changing while observing several of the energy curves, and occasional tremors caused by an unbalanced reciprocating engine sometimes prevented an accurate reading of the galvanometer, so that this series should perhaps not be given as great as some of the preceding sets of energy curves obtained with this same fluorite prism No. 1. This series, however, was observed under more favorable conditions than obtained during the latter part of the preceding series. The radiator was the same as in the

TABLE 20

Series 1912, IX—Blackened Radiator, Fluorite Prism No. 1, Water-cooled Shutter No. 1

[Energy Curves, CLXVIII–CLXXVI]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})			$\lambda_{max}T$	$c = \alpha\lambda_{max}T$
			Mean value	Probable error	Number of computations		
		°	μ	μ			
CLXXIV [a]	P?	1175	2.465	±0.004	7	2896	14 381
CLXXIII	P	1194	2.431	.002	4	2900	14 401
CLXXV	P	1277	2.272	.003	5	2901	14 405
CLXXII	P	1302	2.232	.002	4	2906	14 429
CLXXVI	P	1353	2.153	.001	7	2913	14 462
CLXXI	P	1377	2.114	.001	7	2911	14 456
CLXX	P	1451	2.010	.002	7	2916	14 477
CLXIX [a]	P	1452	2.007	.003	2	2914	14 467
CLXVIII [a]	P	1540	1.890	.003	2	2909	14 443
Mean...	....	....	....	....	....	2909	14 436

[a] Poor curves, sensitivity changing.

preceding sets (Nos. 7 and 8), the break in the platinum ribbon having been repaired, and the optical system having been readjusted before the observations were resumed. A geometrical diagram of the optical path of the radiations shows that, owing to the large opening in the water-cooled diaphragm, it is possible for radiations from the walls of the furnace to enter the spectrometer slit. However, the higher humidity and other difficulties encountered in this series of observations were probably sufficient to mask any errors resulting from extraneous radiations. This series of energy curves gives very uniform results, just as though the increased humidity within the spectrometer box had not been deleterious.

The data of this series are given in Table 20, the mean value being $C = 14\,436$.

IX. SUMMARY

The present paper gives data relating principally to the determination of the mathematical form of the isothermal spectral curve of a black body, and to the computation of the numerical values of the constants relating thereto, for the temperature range between 450° and 1525° C.

This paper contains also data on various subsidiary problems such as (1) the variation of the reflecting power of silver with angle of incidence and with wave length, (2) the variation of reflecting power of fluorite with angle of incidence and with wave length (refractive index), (3) data on the most reliable refractive indices of fluorite, reduced to 20° C, and (4) data for reducing the observations from prismatic to normal spectrum.

The spectrum was produced by means of a mirror spectrometer and a fluorite prism. A vacuum bolometer was used for measuring the partition of energy in the spectrum. The radiator was a porcelain tube, wound with platinum ribbon through which electric current was passed. The various incidental questions such as the adjustments of the optical parts of the apparatus, the temperature uniformity and control of radiator, the water-cooled shutters, the temperature scale, the method of reduction of the observations to the normal spectrum, the proper formulæ for computing the numerical constants, etc., are also discussed.

In a brief summary the results of previous investigations made with similar apparatus are discussed. It is shown that by the elimination of certain errors in the calibration of the prisms used, the older observations are not in disagreement, as was supposed from the published results. It is also shown that, if these older data had been computed by the methods employed in the present paper, the numerical values of the constants would, without doubt, be in very close agreement with the present results. These older data (properly weighted) are therefore used in connection with the present-day results, to form an estimate of the most probable value of the constants of spectral radiation.

The results obtained in the present investigation are based upon experiments with different bolometers, water-cooled shutters, fluorite prisms, thermocouples, and (blackened and unblackened) radiators. It is felt that what success has been attained is owing to blackening the radiator, to properly insulating the thermocouples within the radiator, to placing a knife-edge support beneath the inner radiator to prevent it from sagging, and to projecting an image of the radiating diaphragm upon the spectrometer slit. It is shown that the percentage of the total number of energy curves which fit the Planck equation is increased by blackening the radiator.

About 75 per cent of the reliable energy curves fit the Planck equation, the validity of which was assumed in order to compute the radiation constants from the observed data. This involves a temperature range greater than 1000°. Within this temperature range there is a tendency for the constants to increase slightly with temperature, in several sets of observations, but owing to the various difficulties involved in the work, this slight variation is not sufficiently systematic to be considered an actual departure from the theoretical (Planck) law, upon which the computations are based.

In Table 21 are assembled the reliable data which form the basis for obtaining a mean value of the radiation constants. The mean value of these eight sets (which among themselves contain the mean values of 94) of the best spectral energy curves is:

$$C = 14\,456 \pm 4 \text{ mikron deg.}$$
$$A = 2911 \pm 1 \text{ mikron deg.}$$

The mean value of these 94 energy curves, taken as a single group, hence giving the same weight to each curve, is $C = 14\ 458$. The mean value of all energy curves observed in 1911 and 1912 (the 105 energy curves in the eight sets of observations, not excluding the poor ones) is $C = 14\ 471 \pm 8$. Here the probable error of the result is doubled by including the doubtful curves which should be rejected for the reasons given in the text. However, it is evident that no matter how we combine the observations, it affects but little the mean value of the constant. This is owing to the large number of energy curves, and the large number of computations (4 to 7) made upon each energy curve. The final value is, in fact, based upon about 600 individual values.

TABLE 21

Series	Number of energy curves	Mean value C	Remarks
1911			
I	26	14 469	Unpainted Marquardt porcelain radiator. (Water-cooled shutter No. 2.)
1912			
I	7	14 463	Unpainted radiator as used in 1911.
II	14	14 432	Radiator painted with chromium oxide.
III	7	14 466	New unpainted Marquardt radiator.
IV	9	14 446	Radiator painted with a mixture of the oxides of cobalt and chromium.
V	14	14 476	Radiator repainted; optical path readjusted.
VIII	8	14 461	New thermocouples; radiator the same as in the preceding series.
IX	9	14 436	New water-cooled shutter, No. 1; the rest of the apparatus is the same as in the preceding series.

Mean value $C = 14\ 456 \pm 4$ (94 energy curves)
$A = 2911 \pm 1$

The weighted mean value of the four sets of observations mentioned in the text (viz, Lummer and Pringsheim,[56] $C = 14\ 460 \times 1$; Paschen,[56] $C = 14\ 458 \times 3$; Coblentz, $C = 14\ 456 \times 10$; Warburg, $C = 14\ 374 \times 10$) is $C = 14\ 420$ and $A = 2905$. The mean value of the results of Warburg and of the writer is $C = 14\ 415$.

The difference in the results of the two recent determinations causes an uncertainty of about 3° at the melting point of palladium (m. p. = 1549°) and of about 5° at the melting point of platinum (m. p. = 1755°).

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[56] After recomputation as explained.

In conclusion, especial acknowledgment is due Mr. U. F. Rosen for the numerical computations involved in this research.

WASHINGTON, December 12, 1912.[57]

X. NOTE ON THE TEMPERATURE SCALE.

During the past month Dr. Burgess and Mr. Kellberg have made a thorough investigation of the thermocouples used in this research, including a calibration at the melting point (1549°) of palladium. This was done in order to obtain a check upon the accuracy of the temperature scale obtained by extrapolation from the melting point (1083°) of copper, as described on a previous page.

The annealed thermocouples (known as C_2, C_3, C_4) were first calibrated by freezing and melting points in copper, antimony, and zinc. The emfs observed were somewhat lower (equivalent to 0°.5 to 1° in temperature) than the previous calibrations. However, this does not require a correction in the temperatures recorded in this investigation, for in the meantime the thermocouples had been used in determining spectral energy curves produced by a cloudy fluorite prism (to be mentioned presently), after which the radiator was heated above 1500° for some tests with a colorimeter. The high temperatures employed in the latter work were no doubt responsible for the change in the emf of the couples.

A homogeneity test was then made on these couples, one of which showed a contaminated place in the platinum wire. However, since the mean value of the results obtained with this thermocouple are in agreement with the values obtained with the other thermocouples, no apprehension is felt because of this fact.

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[57] This is the date when the writing of this paper was completed and abstracts were issued for publication (J. Wash. Acad. Sci., **3**, p. 10, 1913; and Amer. Phys. Soc. (Phys. Rev. (2), **1**, p. 249, 1913)). As explained in the text (see "Temperature scale") there was a systematic increase in the value of *C* for temperatures above 1400°; and it was necessary to assume this to be a fault in the estimation of temperatures or in the Planck equation. The writer chose the former alternative and modified the corrections to the optical temperature scale. This modification of the temperature scale above 1400° has no effect upon the data obtained in 1912, which is the crucial work, owing to the fact that intentionally (to save the thermocouple calibration, the difficulty with the temperature correction was not foreseen) no energy curves were observed at high temperatures. The systematic errors which formerly caused the mean values of the various sets of observations to differ by 0.2 to 0.5 per cent are now reduced to less than 0.2 per cent. The former values of *C* published in these two journals are therefore withdrawn. Washington, January 15, 1913.

The couples were then annealed by heating them electrically to about 1600° C. The palladium points were then taken on C_2 and C_3 by fusing a small piece of palladium about 5 mm long between the platinum and the alloy wires and melting the palladium in an iridium tube furnace. The couples were then calibrated at the freezing points of copper, antimony, and zinc. The couple C_3 showed no change as the result of annealing. This couple is in close agreement with the Geophysical Laboratory's standard curve given in the American Journal of Science, July, 1910.

The palladium used in this calibration was obtained from Heraeus, and from Day & Sosman of the Geophysical Laboratory. The results from the two kinds of material are in agreement within the limits of experimental error.

As explained in Part IV of this paper, the true temperatures were obtained by adding to the temperatures on the thermoelectric scale certain values given in Table 4. The present data, including the calibration at the melting point of palladium, were obtained to test the accuracy of the temperature corrections given in Table 4. For this purpose the thermocouple calibration curve was computed using zinc, antimony, and copper as the three fixed points. The calibration curve was computed also by using antimony, copper, and palladium as the fixed points. The difference between the calibration curve extrapolated beyond the copper fixed point and the calibration curve obtained by interpolation between the copper and the palladium fixed points gives the true temperature corrections. The results obtained with the two thermocouples show that the corrections in Table 4 are too small at the lowest temperatures (1,200°) and too large at the highest temperatures. The correction is about 2° at 1,200° and about 8° at 1,400°. Making these corrections in Tables 11 to 20, inclusive, has but little effect on the final mean value. For example in Table 21 the mean values of C taken in succession are to be increased by the following values: 22, 4, 14, 7, 2, 9, 0, 14. This increases by 9 the mean value (C = 14,456) of the 8 sets of observations, so that the corrected mean value is

$$C = 14{,}465.$$

The results show that these corrections have but little effect upon the final mean value.

The latest results of Hoffmann & Meisner[58] on the ratio of brightness of two black bodies at the melting points of gold and of palladium, using an optical pyrometer, gives a value of C = 14,440. The value now commonly used is C = 14,500, and from present indications there appears to be no need of haste in adopting a new value.

In conclusion it is desirable to record the results of an investigation made during the past year of the shape of the spectral energy curves obtained with a new fluorite prism having faces 30 by 34 mm. and an angle of 60°. The prism was white and had several streaks of cloudiness but no internal cleavage faces. The energy curves seemed distorted similar to the ones recorded for prism No. 2, mentioned in this paper, and the constants were as high in value as those found for the latter prism (see Table 17). It therefore appears that the homogeneity of the prism is an important factor in determining the shape of an energy curve.

WASHINGTON, October 9, 1913.

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[58] Zeit. für Instrumentenkünde 33, p. 157, 1913.

MELTING POINTS OF THE REFRACTORY ELEMENTS—I. ELEMENTS OF ATOMIC WEIGHT FROM 48 TO 59

G. K. Burgess and R. G. Waltenberg

The elements included in this list are the iron group—nickel, cobalt, iron, manganese, and chromium—and also vanadium and titanium. In subsequent papers results will be given on other refractory elements now being studied, and it is hoped eventually to include all the available refractory elements in this series of melting-point determinations.

The method mainly used is that of the micropyrometer[1] which, for those metals for which the melting is sharp, as nickel, cobalt, and iron, permits working to a precision of 1° or 2° with a few thousandths of a milligram of the material the melting point of which is sought.

An estimation of the melting points of the iron group elements[2] was made some years ago by a similar but less sensitive method at a time when none of these melting points was well known. The object of these earlier measurements was primarily to demonstrate the convenience and reliability of the method, especially for those elements which can be obtained pure only in minute quantities. It is believed that the present series of determinations, with the improved apparatus, will contribute to a more exact knowledge of these melting points.

The melts were taken for the most part in pure hydrogen generated from "hydrone," and further purified and dried by passing, in the order named, through a neutral lead nitrate aqueous solution with lead sulphate in suspension to remove sulphur and arsenic; through a solution of sodium hydroxide to remove carbon dioxide, over fused calcium chloride for preliminary drying, over a platinum catalyzer, consisting of a spiral of 0.4 mm platinum wire 1 m long, heated electrically to incandescence to combine the oxygen in the hydrogen and remove arsenic and antimony. It was finally dried by passing through a U tube containing calcium chloride, through concentrated sulphuric acid, and over phosphoric pentoxide. Although this complete train may not be necessary for all the metals studied, yet in some cases, such as chromium and zirconium, pure, dry hydrogen appears essential to success. For the more readily oxidizable metals, it was also found advisable, before admitting hydrogen, to first remove all air from the cold furnace with a vacuum pump.

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[1] A Micropyrometer, by G. K. Burgess, Jl. Washington Academy, 3, p. 7; 1913. Phys. Zs., 14, p. 158; 1913. This Bulletin, 9, p. 575; 1913.

[2] Melting Points of the Iron Group Elements by a New Radiation Method, by G. K. Burgess. This Bulletin, 3, p. 345; 1907.

The melts, except for titanium, were taken on platinum strips 6 to 8 cm long, 4 mm wide, and 0.01 or 0.02 mm thick. Manganese was also melted on nickel strips and titanium was melted on iridium strips. The melting points of nickel, cobalt, and iron were also taken in crucibles.

Calibration with Nickel and Palladium.—For melts on platinum the pyrometer was calibrated in terms of the melting points of nickel and palladium. The melting of these metals is extremely sharp on platinum and they appear to show no alloying until they melt. It is assumed that they melt on platinum at the same temperatures as in crucibles, which we have found to be the case within the limits of observational errors, for nickel, cobalt, and iron, the only metals thus compared.

Numerous observations were made with various metals upon the possible effects on the melting-point determinations of alloying with the platinum strip. We are convinced that except possibly in some cases, which we shall not consider here, in which there may be a chemical reaction among the materials in the furnace, as, for example, when silicon, platinum, and hydrogen are together, there is no significant alloying effect with the apparatus and materials as we use them. We may mention, for example, that with gold on a platinum strip it is possible to have two adjacent pieces of gold, differing in temperature by only 1°, one of which is completely liquid and the other showing no signs of melting. (See Fig. 104.) Again, the alloying of silver with platinum may be examined and followed very readily under the microscope, since the silver appears black before and also just after melting, and only begins to brighten, due to alloying, after melting has occurred, even with very minute particles of silver on the platinum strip. Finally, Day and Sosman find that anorthite and palladium melt in crucibles at the same temperature. We find this also true for the melting of these substances on platinum. Moreover, we have exactly reproduced with the micropyrometer their value of the diopside melting point, 1391, with some of their material; thus proving that calibration with metals gives correct melting points of nonmetallic materials.

The melting points of both nickel and palladium may be considered as well established by several series of measurements, in particular by the gas thermometer measurements of Day and Sosman.[3] The palladium point has also been determined several times by optical methods,[4] and the difference between nickel and palladium has been carefully measured.[5]

We have made an independent optical determination of the nickel melting point in hydrogen with an Arsem furnace.[6] The nickel was melted in a magnesia crucible contained within an outglazed closed-end porcelain tube or one of kaolin. Temperatures were measured with a Holborn-Kurlbaum form of Morse pyrometer which had been calibrated by Dr. Kanolt at the melting points of antimony (630), Ag_3-Cu_2 (779), silver (960.5), copper (1083), and diopside (1391). Five observations by Dr. Kanolt on the melting point of platinum with this pyrometer gave 1755 ± 5 in an iridium furnace, or in exact agreement with the generally accepted value.[7]

For nickel, four observations in hydrogen gave us 1449, 1450, 1449, 1449 in the Arsem furnace, by the method of optical heating and cooling curves,[8] which is close to Day and Sosman's value, 1452. Four observations of the melting point of nickel on iridium with the micropyrometer gave us 1452.

With the long-filament pyrometer lamps used, the equation[9] $\log C = a + b \log T$ (in which C = current, T = absolute temperature, and *b* is very nearly unity) is sufficient for very considerable temperature ranges, and permits a calibration in terms of two temperatures only, i. e., nickel and palladium. Applying this equation by extrapolation to the determination of the platinum melting point by observing the melting of platinum strips mounted as usual for taking metal melts, we obtained 1755° ± 5 from six observations. The relatively small precision is due in part to the impossibility of perfectly controlling the rheostats and exactly matching lamp and strip at the instant the latter burns out and in part to the fact that the strip does not always melt at exactly the spot sighted upon.

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[3] Day and Sosman, Carnegie Institution of Wash. Pub. No. 187; 1911.

[4] Waidner and Burgess, this Bulletin, **3**; p. 163; 1907. Warburg and others, Berlin Akad , p. 35; 1913. Nernst and Wartenberg, Verh. Deutsch Phys. Ges., **8**; p. 48; 1906.

[5] Ruer, Zs. Anorg Ch., **51**; p. 223; 1906.

[6] J. Am. Chem. Soc., **28**; p. 921; 1906.

[7] See Day and Sosman, loc. cit.; Waidner and Burgess, loc. cit.

[8] C. W. Kanolt, Techn. Paper No. 10, Bureau Standards; 1912.

[9] Pirani, Verh. Phys. Ges., **12**; p. 323; 1910.

We had originally intended to adopt a three-point calibration, and expected to use for this purpose nickel, cobalt, and palladium as determined by Day and Sosman, but we found it impossible to make the value of the cobalt point as determined by them fit the curve by some 10°, as will be shown later, and fortunately the two-parameter curve was found sufficiently exact.

The metals actually used for calibration in hydrogen were "Kahlbaum" electrolytic nickel (M. P. = 1452) and pure Heraeus palladium (M. P. = 1549), both of the same grade as used by Day and Sosman.[10] A sample of their palladium gave exactly the same melting point as ours. Palladium melts at the same temperature in air, vacuo, and hydrogen, according to our observations. In controlling the constancy of the pyrometer lamps and studying the reproductibility of the melts some 35 observations were taken of nickel and 20 of palladium. The various metals were not studied in regular order but mixed as indisciminately as possible, with observations on the standard points, nickel and palladium.

IRON

Pure electrolytic iron from three sources and as many different methods of preparation was used, namely, from Prof. C. F. Burgess (same iron used in the 1907 observations [11]) from Langheim-Pfanhauser Werke A. G. kindly furnished by Dr. Hans Goldscmidt, and

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[10] Day, Sosman, and Allen, loc. cit. The analysis by Dr. Allen of these products gave the nickel as 99.835 pure and the palladium 99.975.

[11] G. K. Burgess, loc. cit.

Mr. Wm. C. Cuntz, and from a sample prepared by Mr. J. R. Cain, of this Bureau. The analyses as furnished are as follows, not including gases:

	C. F. Burgess	Langheim-Pfanhauser	Cain
	Per cent	Per cent	Per cent
Sulphur	0.00	0.00	0.004
Silicon	.013	.00	.001
Phosphorus	.004	.007	.0006
Manganese	.00	.00	.0000
Carbon	.012	.00	.004
Copper	...	.008	.008

"Kahlbaum" iron in powdered form and iron reduced on the platinum strip in hydrogen from "Kahlbaum" oxide were also used.

In Table 1 are given the results obtained in a hydrogen atmosphere with the micropyrometer.

TABLE 1

Melting Point of Iron by Micropyrometer

Electrolytic, C. F. Burgess	Electrolytic, Langheim-Pfanhauser	Electrolytic, Cain	Powder, "Kahlbaum"	From oxide, "Kahlbaum"
1538	1524	1533	1534	1532
1537	1532	...	...	...
1530	1534	...	...	...
1534	1534	...	...	...
1530	1535	...	...	...
1532	...	...	...	...
Mean, 1534	Mean, 1532	...	...	...

There appears to be no systematic difference among the several samples nor for different sized pieces, and the mean value is 1533 ± 1. This is somewhat higher than all other recent determinations. Carpenter, for instance,[12] assigns the value 1520 and in Landolt's tables (4th ed., 1912) the range is 1502 to 1532.

We venture to suggest that this apparently high determination of the iron point furnishes further evidence that the method here used does not give low results for metals alloying with platinum, even in those cases in which the addition of either metal to the other is known to lower the melting point as is the case for iron-platinum.

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[12] H. C. H. Carpenter, Iron and Steel Inst.; September, 1908.

The melting and freezing points of iron, in vacuo and in hydrogen, were also taken in the Arsem furnace. Four observations in vacuo gave 1531, 1531, 1529, 1527, and two in hydrogen gave 1523, 1527.

COBALT

The cobalt used was cobalt "Kahlbaum" in the form of powder, Kahlbaum's würfeln, cobalt reduced in hydrogen on the platinum strip from "Kahlbaum" cobalt oxide, and a sample kindly furnished by Messrs. Day and Sosman, cut from material which had actually been used for their determinations and which was originally powdered cobalt "Kahlbaum" [13] shown by Dr. E. T. Allen to be 99.951 per cent cobalt.

The cobalt "Kahlbaum" and würfeln were observed simultaneously and no appreciable difference in their melting points was detected.

TABLE 2

Melting Point of Cobalt by Micropyrometer

"Kahlbaum" powder and würfeln together	Co from the oxide "Kahlbaum"	Day and Sosman's sample
1478	1475	1474
1479	1478	1478
1482	....	1478
1476	....	....
1475	....	....
1476	....	....
1478	....	....
Mean, 1478	....	....

All these samples appear to have the same melting point, the mean value of which is 1477 ± 2. Three observations taken in the Arsem furnace, by the same method described for nickel, each gave for the melting point of cobalt 1478. Finally, two melts of cobalt on iridium gave with the micropyrometer 1477 and 1478.

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[13] Day, Sosman, and Allen, loc. cit.

The value of the cobalt point which Day and Sosman found is 1490 in a nitrogen atmosphere. They used powdered cobalt heated in crucibles of 22 cc in hydrogen, the nitrogen replacing hydrogen immediately preceding an observation. They consider their cobalt determinations less satisfactory than those of nickel. There is a possibility of oxidation of some of the powder which may be sufficient to raise the melting point (cf. chromium and vanadium). We hope later to be able to study the effects of the presence of oxides on the melting points of the iron-group elements.

CHROMIUM

Strictly pure chromium was not available, and it is difficult to locate exactly the melting points of an impure viscous substance. Observations were taken on two samples from Kahlbaum and on one from Dr. H. Goldschmidt, all of a purity probably not greater than 98 per cent.

TABLE 3

Melting Point of (98 Per Cent ?) Chromium by Micropyrometer

Kahlbaum I	1527
Kahlbaum II	1536, 1513, 1513
Goldschmidt	1514, 1524

As best representative value we may take 1520, or a temperature slightly lower than the iron melting point, 1533. However, the melting point of pure chromium may well be above that of iron, as is shown by a consideration of the formula for lowering the freezing point by metallic impurities:

$$\Delta t = \frac{0.02 \;.\; T^2 \;.\; p}{\rho \;.\; M}$$

when p = per cent impurity of molecular weight M, ρ = heat of fusion at absolute temperature T. Assuming that $\rho = 30$ and $M = 100$, we have $\Delta t = \frac{0.02 \;.\; \overline{1800}^2 \;.\; 2}{30 \;.\; 100} = 43°$, so that assuming this formula to hold, which is questionable, the melting point of strictly pure chromium might be as high as 1560. On the other hand, the value 1520 may be nearer the true one if, as appears probable, the presence of oxides acts in the direction not of lowering but of raising the chromium melting point, as was found in the case of vanadium by Ruff and Martin.[14] If chromium is melted, for example, in a slightly oxidizing atmosphere or in impure hydrogen, an apparent melting point above that of platinum may be obtained.

MANGANESE

We have not been able to obtain pure manganese, and the impure samples from Kahlbaum and from Goldschmidt are even more sluggish than chromium. The Goldschmidt manganese was from a sample furnished with the following analysis:

	Per cent.
Si	0.70- 1.00
Fe	.95- 1.05
Al	.40- .70
S	.05- .10
P	.20- .30
Mn	97.70-96.90

Melts were taken both on platinum and on nickel strips with the micropyrometer using gold (1063) and palladium as calibration points. Those on nickel were less satisfactory, due apparently to evaporation of nickel.

TABLE 4

Melting Point of (97.5?) Manganese

Kahlbaum		Goldschmidt	
On Pt	1242	On Pt	1261
On Ni	1221	On Pt	1264
		On Pt	1279
		On Ni	1254

The mean is 1254, which is possibly lower than the melting point of strictly pure manganese by 20°.

VANADIUM

Dr. v. Wartenberg, of Berlin, was kind enough to send us some 97 per cent vanadium prepared by him from the suboxide by the alumino-thermic method with calcium. It contains traces of Ca, Al, and Fe. Prof. Wedekind, of Strassburg, also furnished us with a sample of his 98 per cent vanadium.

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[14] Ruff and Martin, Über reines Vanadin Zs Angew. Chem., **25**, p. 49; 1912.

We have also examined two samples purchased from Kahlbaum at different dates. None of the samples melt sharply, the substance being quite viscous, and they all show evidences of incipient melting many degrees below the temperature at which the melting is complete.

With the Kahlbaum samples, evidences of melting were apparent as low as 1500 and melting was complete at about 1720, the samples showing evidences of nonhomogeneity of composition.

With Dr. v. Wartenberg's and Prof. Wedekind's vanadium the following results were obtained:

TABLE 5

Melting Point of Vanadium by Micropyrometer

98 per cent Va from Wedekind	97 per cent Va from v. Wartenberg	
1700	1680	Pieces of about 0.001 mg
1757	1691	
1773	1691	
1717	1685	
	1699	Medium sized pieces
	1705	
	1725	Largest pieces

Evidences of incipient melting were apparent from about 1650 with both of these materials, and the vanadium of Prof. Wedekind appeared to be somewhat inhomogeneous.

Other determinations of the vanadium melting point are as follows:

Year	Author	Method	Va M. P.
1905	v. Bolton	Total photometric	1680
1908	Vogel and Tammann	Optical and thermoelectric Va containing 1.2 per cent Si	1750
1910	v. Wartenberg	Optical in Tungsten furnace 97 per cent Va	1710
1912	Ruff and Martin	Optical, from oxides and carbide in solution	1715

According to the experiments of Ruff and Martin,[15] the presence of either an oxide or the carbide raises the vanadium melting point. As some oxide is usually present, its effect probably neutralizes the lowering due to the slight amount of metallic impurities. We would place the vanadium melting point at about 1720, both from a consideration of our own and of other determinations.

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[15] Ruff and Martin, loc. cit.

TITANIUM

Prof. M. A. Hunter, of the Rensselaer Polytechnic Institute, was kind enough to place at our disposal a sample of pure titanium which he prepared from material furnished by the Titanium Alloy Manufacturing Co., of Niagara Falls. This titanium as analyzed by Prof. Hunter contains only a trace of iron and no other detectable impurity. Prof. Wedekind likewise kindly sent us two samples prepared by him and one by Dr. v. Wartenberg. The colloid titanium of Wedekind melted at 1503 to 1451, and his powdered titanium at 1452.

We also took observations on two samples from Kahlbaum, which were evidently from their behavior quite impure, showing evidences of considerable inhomogeneity and an extended melting range. For the Kahlbaum samples the following points were obtained: 1664, 1724, 1677, 1737, 1641.

The titanium of Hunter and of v. Wartenberg showed no signs of melting on platinum. The melting points of these samples were taken on iridium strips.

TABLE 6

Melting Point of Titanium by Mycropyrometer

Ti from Prof. Hunter	Ti from Dr. v. Wartenberg
1790	1778
1785	1807
1785	1815
Mean, 1787	Mean, 1800

These melting points are fairly sharp, and the location of the temperature was made by calibrating the micropyrometer for the iridium strip by taking observations on it of the melting of palladium (1549) and of platinum (1755).

SUMMARY

We have shown that the micropyrometer may be made an instrument of precision for the determination of the melting points of refractory metals and salts; that in the case of the metals examined the effect of alloying of microscopic particles on platinum and iridium is inconsequential until after melting, which we have shown for nickel, cobalt, and iron to occur at the same temperature for minute particles on the strips as for considerable quantities in crucibles of magnesia.

Assuming the melting points of nickel to be 1452, palladium 1549, and platinum 1755, and the calibration curves of the pyrometer lamps of the form $\log C = a + b \log T$, for the range here studied, we have determined the melting points of Fe, Co, Cr, Mn, Va, and Ti with the micropyrometer and of Ni, Co, and Fe in quantity in the electric furnace, all melts having been taken in pure hydrogen and Fe also in vacuo. For Cr, Mn, and Va, strictly pure materials were not available, and we can but estimate the melting points of the pure elements.

TABLE 7

Melting Points of Elements of Atomic Weight 48 to 59

Metal	Melting point with micropyrometer	Purity	Probable melting point of pure element
Nickel	[16] 1452 [17] 1449	99.83_5	1452±3
Cobalt	1477±2 [18] 1478±1	99.95_1	1478±5
Iron	[19] 1533±1 [17] 1528	99.98±.01	1530±5
Manganese	1255	97–98	1260±20
Chromium	1520	98–99	1520 to > Fe?
Vanadium	1720	97–98	1720±30
Titanium	1794±12	99.9+	1795±15

[16] Assumed value on platinum strip; also observed value on iridium strip.

[17] Crucible melts in electric furnace.

[18] Crucible melts in electric furnace; also on iridium strip with micropyrometer.

[19] Five samples all agreeing to within 3°.

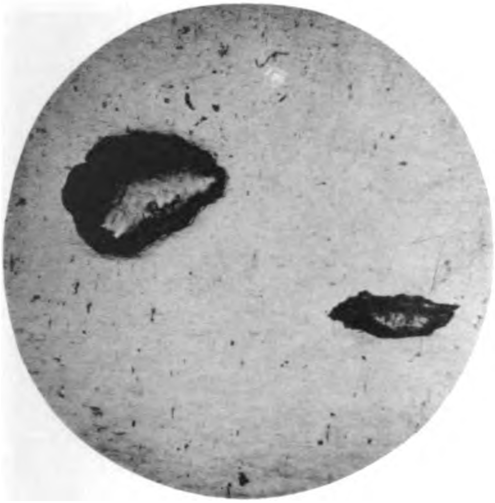
PHOTOMICROGRAPHS

The photomicrographs show the appearance of the material on the strips as it is taken out of the apparatus. The photographs of the cold strip were taken with a metallographic microscope using vertical illumination and a magnification of 25 diameters.

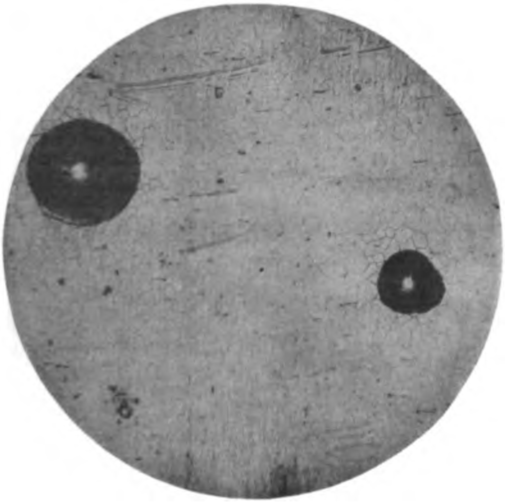
Photomicrograph No. 104 shows two pieces of gold separated by less than 1 mm, one melted the other not melted. The pieces were about the same size when put on the strip but the piece which had been melted appears larger because it flattens on melting. The difference in temperature between the pieces was probably less than 1° C and the temperature of the strip was held constant while several observations were recorded. We consider this to be an indication that alloying between the strip and a metal on the strip does not have any appreciable effect on the melting point of the metal.

The streaks appearing in micrograph No. 87, Kahlbaum titanium on a platium strip, and No. 90, vanadium, are typical of impure substances. No such streaks have been observed with pure metals, but those elements which we know are pure gather into globules, as is shown in the micrographs of nickel, iron, and palladium.

WASHINGTON, April 25, 1913.



NO. 104. GOLD. X 25.



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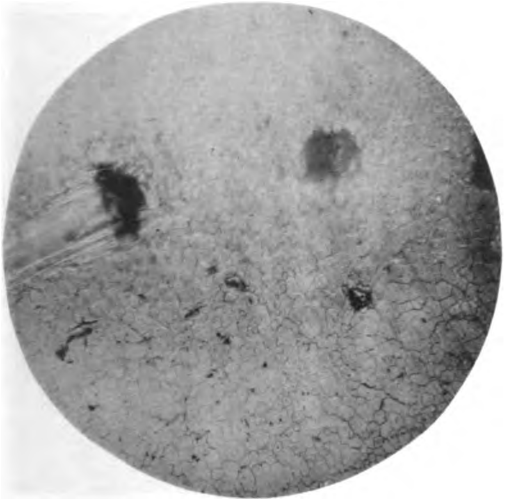

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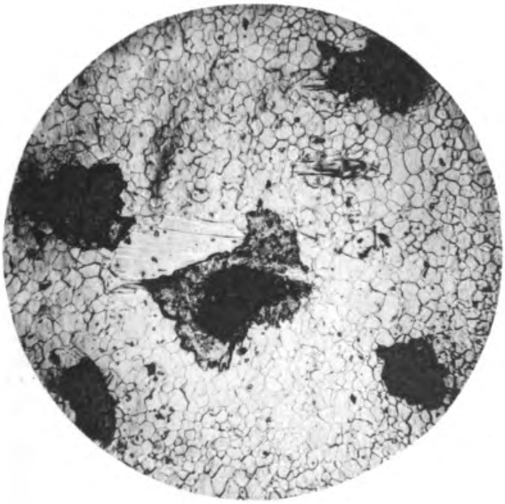

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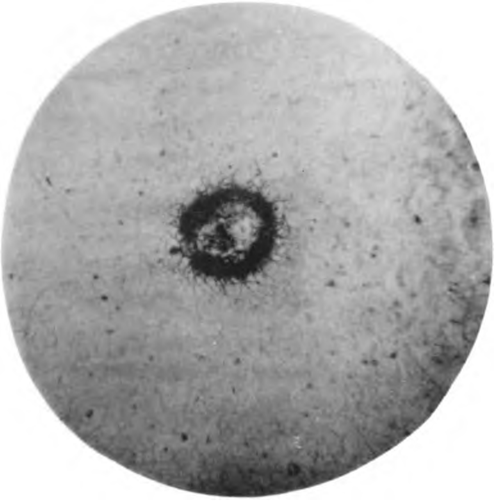

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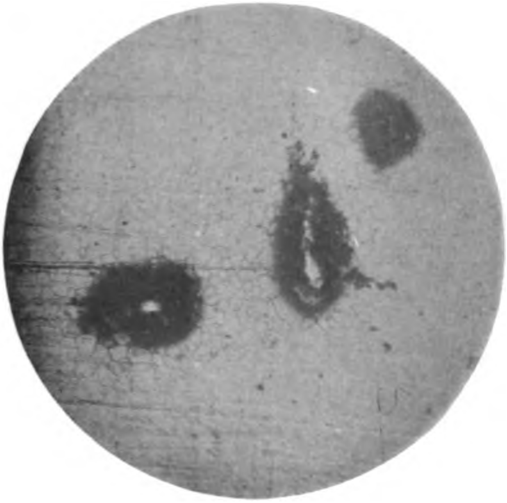

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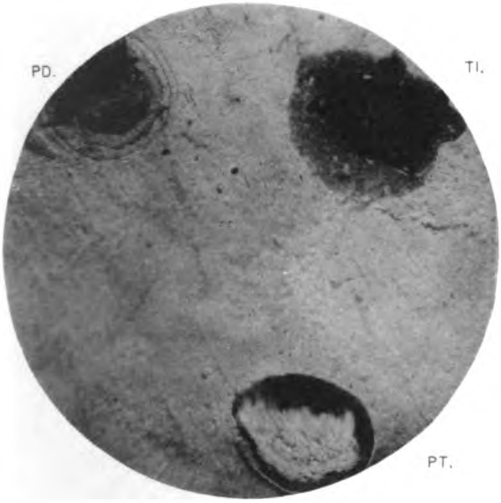
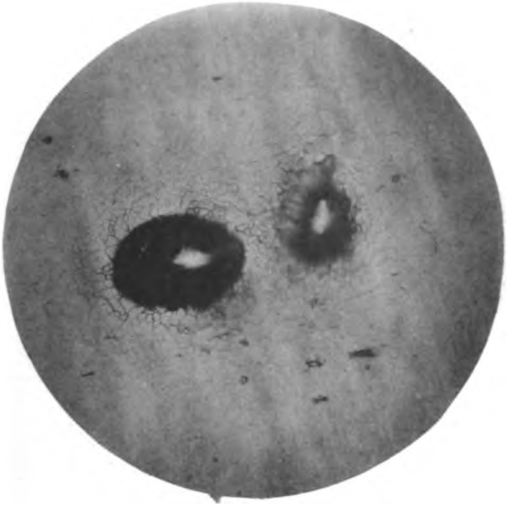


NO. 426. PALLADIUM PLATINUM TITANIUM } ON IR. X 25



NO. 437. PALLADIUM. X 25.

HIGH-FREQUENCY AMMETERS

By J. H. Dellinger

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I. INTRODUCTION

1. SCOPE OF INVESTIGATION

Instruments for the measurement of current of radiotelegraphic frequencies, about 100 000 to 2 000 000 cycles per second, generally depend upon the thermal effect of the current. The electrodynamic effect of the current has not been very successfully utilized; because when the wire is coiled up to form an electrodynamometer, conditions are favorable (impedance large and capacity large) for part of the current to flow through the dielectric instead of the wire, in amount varying with the frequency. An electrodynamic instrument which is useful for some purposes utilizes the eddy currents in a conducting ring suspended within a coil [1] which carries the current to be measured; however, the deflection varies with frequency, so that the instrument can not be considered in the usual sense an ammeter. The thermal effect, on the other hand, can readily be measured in a simple straight wire as well as in any other form of circuit, so that a suitable form of circuit is most readily attained in the thermal ammeter. The heat production may be measured by any thermometric method, and the following are in use: Expansion, calorimetry, change of electric resistance, and thermoelectric effect.

Observation of the heat production in a simple single wire is by no means a complete solution of the high-frequency ammeter problem. Consider the equation:

$$H = RI^2, \tag{1}$$

in which H is the rate of heat production, R is the resistance, and I is the effective current. The indicated current in any thermal ammeter depends upon H. It is well known that the resistance of any conductor increases as the frequency of the current increases, hence in general the indicated current will vary with frequency. For this change to be negligible, the conductor must be of smaller and smaller cross section as the frequency is increased. For the frequencies under consideration, this error will be greater than 1 per cent unless the diameter of the wire is less than a few tenths of a millimeter. Still there is nothing serious about this if only small currents are to be measured. But when larger currents than about 3 amperes have to be measured, the single wire will not suffice; the wire must be of so small a diameter that its resistance is not changed by frequency, but then the large currents will overheat it, i. e., alter its properties. To measure large high-frequency currents, therefore, the current must have more than one path, and it is common to use (*a*), wires in parallel, (*b*), different portions of the same wire in parallel, or, (*c*), broad, thin strips of metal.

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[1] J. A. Fleming: "The principles of electric wave telegraphy," p. 201; 1910. G. W. Pierce: Phys. Rev. **20**, p. 226; 1905.

It is a common dictum that ammeters used in measuring currents of even moderately low frequency must not be shunted. This is obvious from consideration of the expression relating the current I_1 in the instrument and I_2 in the shunt, neglecting mutual inductance,

$$\frac{I_1^2}{I_2^2}=\frac{R_2^2+p^2L_2^2}{R_1^2+p^2L_1^2},$$

since usually the inductances of the instrument and the shunt are in a different ratio from that of the resistances, and hence the distribution of the current varies with frequency. In fact, even if $\frac{L_2}{L_1}=\frac{R_2}{R_1}$, the current distribution in an actual case is likely to vary with frequency because of the mutual inductance. Now, any high-frequency ammeter in which the circuit within the ammeter itself consists of more than a single elementary filament—or its closest approximation, a fine wire—in reality involves shunting, and needs most careful consideration before it can be pronounced free from error. When the indicated current depends on the heat production in just one branch of such an instrument the error due to change of current distribution on high frequencies may be very great. When the indicated current depends on the heat production of the whole current, the error will be of a smaller order of magnitude, but may be appreciable when the change of current distribution is great, inasmuch as the total heat production in any system increases as the distribution on direct current is departed from. The increase of total heat production is equivalent to an increase of R, the resistance of the system as a whole, in equation (1).

It has been known for some time that most of the ammeters in common use for measuring large high-frequency currents are subject to large errors. Users of the ammeters have put a number of them in series in high-frequency circuits and have been puzzled at the divergence of their readings. Various sources of error have been suspected, namely, change of current distribution, resistance change, eddy currents, capacity, and inductive action from other portions of the circuit. It was the purpose of this investigation to sift out these possible errors and to determine the magnitudes of the effects that need to be considered in high-frequency current measurement. This has involved a critical study, experimental and theoretical, of typical ammeters at various frequencies. The investigation includes more than what is usually connoted by the term "hot-wire" ammeter, viz, the commercial expansion instrument. It includes all the instruments whose indications depend on the thermal effect of the current, some of which are capable of high precision.

2. NEED FOR THIS WORK

There is great practical necessity for reliable ammeters in high-frequency work. A hot-wire ammeter is found in every radio station, and in some stations high-frequency currents of 300 amperes are used. The Government inspectors charged with enforcing the laws regulating power radiation must have portable ammeters upon which they can rely. The measurement of current is far more of a cardinal operation at high frequency than on direct current, for there is no potentiometer for precise measurement of high-frequency electromotive force and no Wheatstone bridge for precise measurement of high-frequency resistance. The design of resistances to carry large high-freqeuncy currents involves the same principles as the design of the circuits in ammeters. In the present state of high-frequency measurements great accuracy is not required, but it is at least desired to have current measurement correct to 1 per cent.

3. PLAN OF TREATMENT

The apparatus used and the experimental procedure will first be described, and then the three main types of ammeter will be treated in order without reference to experimental details. The means of measuring the heat production in the ammeter is a thermometric problem, affecting the precision and not necessarily the accuracy of the instrument; this investigation deals primarily with the electrical problem, or the form of the circuit within the ammeter. The experimental results obtained will be presented along with the theoretical discussion of each type. This is done because the main interest of the work lies not in the particular results here obtained, but in their illustration of the principles which govern the performance of high-frequency ammeters.

II. EXPERIMENTAL PROCEDURE

The general method of experiment was to observe simultaneously the thermal effects in the ammeter under test and in an ammeter which could be considered standard, the two being in series, using alternately high-frequency and low-frequency current. Any low frequency was equivalent to direct current, because the effects under investigation became appreciable only at very high frequencies, as will be shown.

1. CIRCUITS

The high-frequency current was produced by the oscillatory discharge of condensers; and the low-frequency current was obtained from an ordinary generator. The condensers were of the Leyden jar type, and the inductances were the open-coil type used in radiotelegraphic work. A diagram of the apparatus is given in Fig. 1. A is an induction coil, supplied with 60-cycle alternating current; it is, in other words, a transformer for high voltages. The spark gap was either a rotating gap giving about

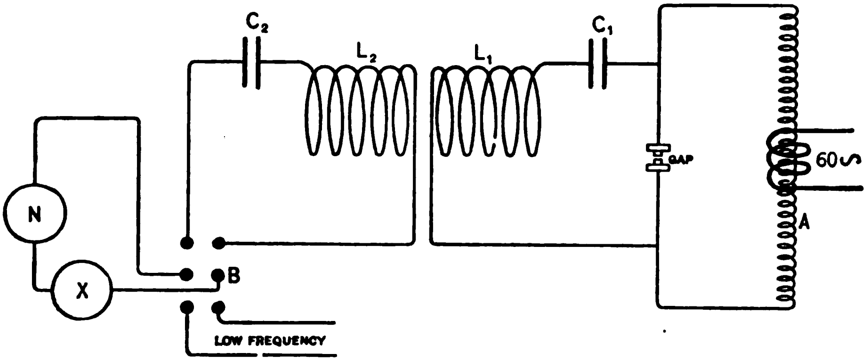

Fig. 1.—*Diagram of apparatus*

500 sparks per second, or a stationary gap with an air blast, using as electrodes small tungsten disks secured in copper and aluminum disks which helped to dissipate the heat. Both forms of spark gap gave sufficiently constant current. In Fig. 1, B is a double-throw switch, enabling either the high-frequency or low-frequency source of current to be connected to the ammeters X and N, one of which was under test and the other was the standard.

Experimenters[2] upon high-frequency resistances have used what purported to be a null method by balancing the thermal effect of X against the thermal effect in a similar auxiliary specimen, X′, carrying direct current. This additional experimental complication did not seem worth while in these experiments, since the observations in any case depend on a deflection, that of N. (To be sure, it could be made more nearly a null method by balancing the thermal effect of N also against an N′ carrying direct current, but this would involve still further experimental complication.) In addition, the thermal effect of X in some cases can not be readily balanced, e. g., in an expansion type commercial hot-wire ammeter.

A secondary circuit (L_2, C_2) was used because it is in similar secondary circuits that high-frequency current is usually measured. The frequency was measured by means of a wavemeter brought near the secondary circuit. The frequencies used were from 100 000 to 1 500 000, because this is the range of frequencies in radiotelegraphy; and furthermore, because it was found that the large and interesting changes of current distribution occur in this range, owing to the inductance becoming a determining factor in the impedance. It was found impracticable to go to higher frequencies, because at 1 500 000 capacity effects began to be appreciable; part of the current went through the dielectric instead of through the wire, so that two instruments in series did not carry the same current. The experiments on this point are given below.

2. STANDARD INSTRUMENTS

In considering the ammeters herein investigated, it must be borne in mind that the requirements are very different from those in the measurement of small currents, in which sensibility is the desideratum. In an instrument for measuring very large currents the problem is, on the other hand, to dissipate the heat produced. The measurement of the heat production presents little difficulty, and in the instruments investigated the thermometric methods employed were expansion, electric resistance, and thermoelectric effect. The expansion of the hot wire or strip was utilized in the commercial ammeters. The electric resistance of the hot wire or strip can be conveniently utilized only in a particular form of instrument, as will be shown. The thermoelectric effect was advantageously employed to measure the current distribution among the parts of experimental ammeters.

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[2] J. A. Fleming: Electrician, 64, p. 381: 1909. H. W. Edwards: Phys. Rev., 33, p. 184; 1911.

For currents up to about 2 amperes a single fine wire served as the circuit of a standard instrument. The wire had to be fine enough so that its resistance was the same at the high frequencies as at very low frequencies. The work proceeds on the assumption that such an instrument is correct at all frequencies. Two such instruments, one having a copper wire and the other a Eureka[3] wire, were compared and found to agree at all frequencies; this, together with the consistency of the results obtained throughout the work, and the quantitative agreement of the effects experimentally obtained with the theoretical calculations, furnish the justification of the assumption. A one-wire instrument, using a thermocouple to measure the heat production, is shown in Fig. 2. A is the fine wire which constitutes the essential part of the instrument. It is soldered to vertical copper rods, mounted on a wooden or hard-rubber base. The current enters the "hot wire" A through these vertical rods at right angles to it. A copper Eureka thermocouple is hard soldered to the middle point of A and connected to the binding posts and

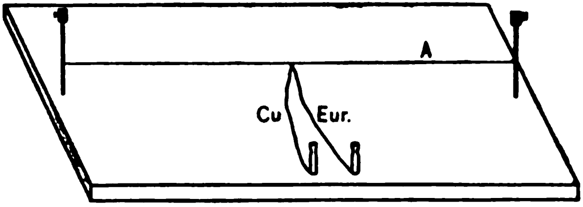

Fig. 2.—*Standard instrument of one wire*

thence to a galvanometer. A cover over the whole instrument protected the hot wire and the thermocouple wires from air currents.

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[3] Eureka, "Advance," "Ia Ia," and constantan, all have practically the same properties.

For the measurement of relatively small currents such an instrument was used in which A was a Eureka wire 0.05 mm in diameter. It was suitable for the measurement of current up to about 0.3 ampere, at which the temperature of A was about 75° C and the emf in the thermocouple circuit was about 3 millivolts. In a Eureka wire of that size the increase of resistance for a frequency of 1 000 000 over the direct-current resistance is readily shown by Kelvin's formula[4] to be exceedingly small, less than 0.001 per cent.

For the measurement of currents up to 1.2 amperes a similar instruments was used in which the wire A was copper, 0.08 mm in diameter. Because of its lower resistivity it could carry more current than the Eureka wire for a given amount of heating, but its change of resistance with frequency is greater. However, the increment[4] of resistance at a frequency of 1 000 000 is found to be less than 0.3 per cent.

To measure currents greater than 1.2 amperes, up to 10 amperes, a two-wire instrument was used as standard. As will be shown theoretically in Section III and experimentally in the fourth paragraph below, two wires in parallel constitute as valid an instrument as one wire, provided the two wires are exactly similar in length, cross section, resistance, and configuration, and are fine enough not to change in resistance with the frequency. A system of more than two wires in parallel, however, is likely to be in error at high frequencies. Even in the case of two wires there is difficulty because of the requirement of exact similarity of the two wires. Wires of very small diameter vary considerably in cross section and hardness, and hence two wires which have apparently the same dimensions and consequently the same self-inductances may have resistances several per cent different. This is a most insidious source of error and is found to affect a number of the instruments investigated in this paper. Because of this possible difference of resistance the current distribution in the two-wire instrument is likely to vary with the frequency, and hence the indications of a thermocouple on one of the wires would not give true current values. If, however, the heat production in the whole instrument be measured, instead of the heat production in one wire only, the instrument is practically free from error; since, as will be shown in Section IV, the change of current distribution is a first-order change, while the change of the total heat production is a second-order change.

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[4] Kelvin: Math. and Phys. Papers, vol. 3, p. 491; 1889. Bull. Bur. Standards, 8, p. 174; 1911.

The total heat production in the two-wire instrument is readily measured by the rise of its electrical resistance when heated by the passage of current. An instrument on this plan was made as follows: Four uprights, bearing copper lead wires, were set in a wooden base at the corners of a rhombus about 10 cm on a side. At points about 3 cm above the base a fine copper wire was soldered as shown. The heating current was introduced by one pair of leads, say L and M, and the resistance was measured between X and Y, these points being connected to a Wheatstone bridge. The fine copper wire was 0.1 mm in diameter. With this it was found possible to measure currents up to 10 amperes by placing the instrument in oil. This method of measuring alternating currents is due to Paalzow and Rubens,[5] and is sometimes called a "bolometer-bridge" method. It has been used[6] as a detector of very small currents of high frequency, making its sensibility very high by putting it in a vacuum. Here current-carrying ability rather than sensibility was desired. This method as a means of measuring large currents of high frequency is believed to be novel.

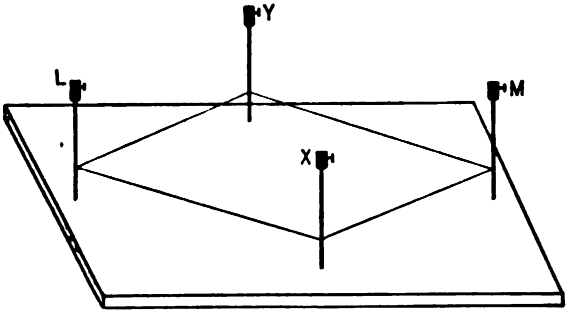

Fig. 3.—*Standard instrument of two wires*

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[5] Wied. Ann., 37, p. 529; 1889.

[6] Tissot (see Fleming: "The Principles of Electric Wave Telegraphy," p. 200; 1910.)

The arrangement for measuring the resistance of the device is shown diagrammatically in Fig. 4. K is a tapping key in the battery circuit. A closed galvanometer circuit was used, thus eliminating errors of false zero. G is a sensitive moving-coil galvanometer. Its sensitivity was such as to permit the 400-ohm bridge arm to be adjusted closer than the limit of precision set by the fluctuations of the high-frequency current. The current through the standard, X Y L M, from the bridge battery was of the order of 0.01 of the heating current, and therefore quite negligible. It was not found convenient to calibrate this standard on direct current, although it is theoretically possible to do so. For a heating current entering at L and M, X and Y need to be so adjusted as to be equipotential points; then no portion of the heating current flows in the bridge used to measure the resistance. However, it is difficult to make this adjustment exactly, and it is moreover unnecessary, as a calibration by low-frequency alternating current is just as good as a direct-current calibration for the purposes of this work. Consequently, the points X and Y were simply made approximately equipotential points, but not adjustable. As seen in Fig. 3, the four leads were perpendicular to the plane of the hot wire, so that there could be no inductive effects between the leads and the hot wire. Some light on the

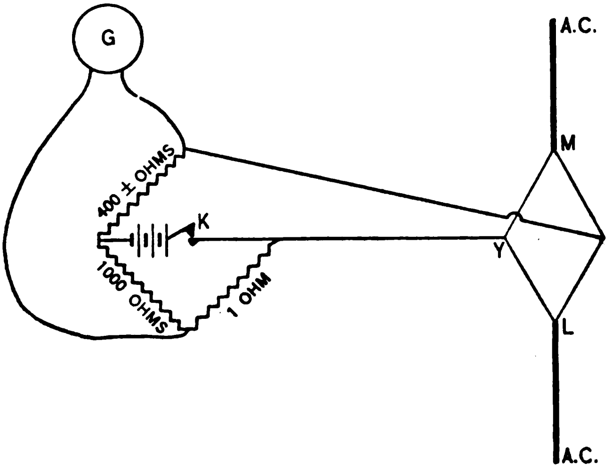

Fig. 4.—*Apparatus auxiliary to the two-wire standard*

possibility of inductive dissimilarities at high frequency could be obtained by interchanging the heating current from the terminals L and M to the terminals X and Y. This was done at the highest frequency for which the instrument was used, 750 000, and no differences could be detected in the results.

Measurement of electric resistance of the heated system is a thermometric method peculiarly applicable to the two-wire instrument. It is readily seen that it can not be conveniently used for systems of other numbers of wires, because of the necessity of keeping the high-frequency current out of the bridge used to measure the resistance.

There is plenty of evidence among the results of this investigation that the thermometric methods used for measuring the heat production do not affect the behavior of the instruments with change of frequency. If certain electrical conditions are satisfied, two instruments agree as well at one frequency as another. For example, the two-wire resistance instrument just described was compared with a one-wire instrument in which the indications were produced by the expansion of the hot wire, at a very low frequency (equivalent to direct current), at 300 000 and at 750 000. As shown by the plotted results, Fig. 5, the two instruments agree throughout. Thus, an answer is obtained to any possible objection to the resistance instrument arising from questionable constancy of the resistance-temperature coefficient of a wire carrying oscillating currents of high frequency (the electrons reversing their direction of drift with great rapidity).

3. TAKING THE OBSERVATIONS

In comparing any two ammeters the experimental procedure was to pass high-frequency current through the two in series for a certain length of time, usually one minute, recording the deflections, then quickly to throw the switch (Fig. 1) from high frequency to low frequency, and allow an approximately equal low-frequency current to flow one minute, recording the deflections; then high frequency again, then low frequency again, and finally high frequency again. Thus, three high-frequency observations were obtained, with two low-frequency observations sandwiched between them. This method of alternating the observations, with the currents run successively for equal intervals of time, eliminated any errors due to thermal or other drifts. A sample set of observations is given in Table 1; the deflections for the "three-wire instrument" being those of a suspended-coil galvanometer, read with lamp and scale, and the deflections of "Standard B" being those of a sensitive pointer-type galvanometer; the galvanometer in both cases measuring the thermocouple current.

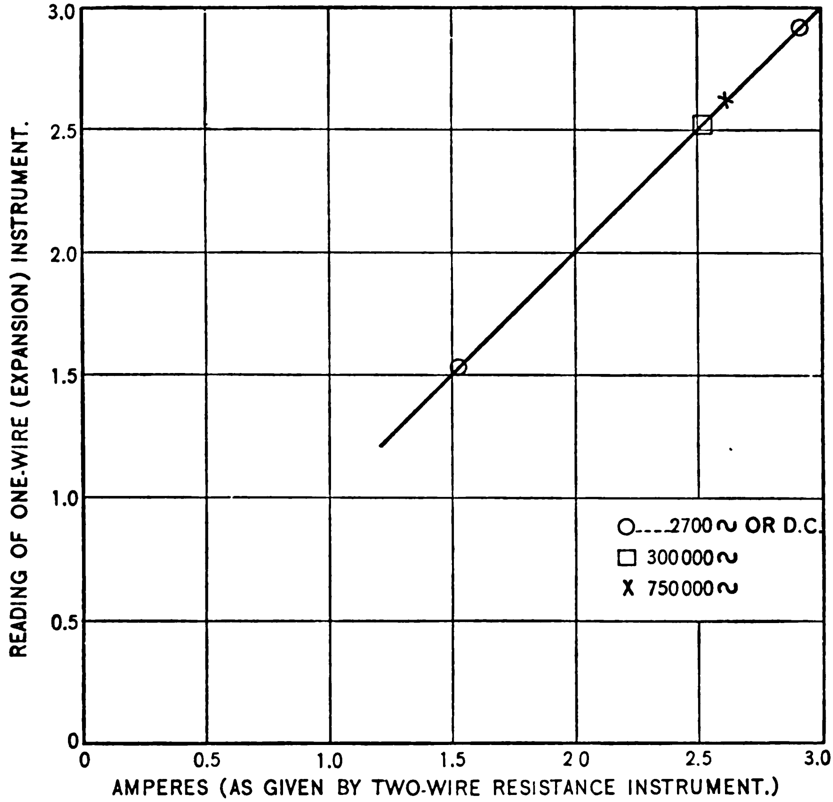

Fig. 5.—*Comparison of two standard instruments*

TABLE 1

Frequency	Three-wire instrument	Standard B
1 500 000	38.0	30.4
60	39.1	28.0
1 500 000	38.2	30.4
60	39.1	27.8
1 500 000	38.9	31.2
Mean 1 500 000	38.37	30.67
Mean 60	39.10	27.90

In some cases, with more than one observer, three instruments in series were simultaneously observed. Instead of estimating the average deflection while the current was on, each observer took the instantaneous deflection and recorded it as many times as he could during the time. The mean deflection is then found arithmetically instead of mentally. A set of such observations is given in Table 2; the observations given under "two-wire standard" are the resistances in the variable arm of the measuring Wheatstone bridge; and those under the other two instruments are the currents indicated on their scales. The data give a good idea of the degree of constancy of the current.

The calibrations of each instrument with respect to a standard instrument, and of the experimental standards with respect to a laboratory standard ammeter, at a low frequency, were plotted. By interpolation from these curves, and from the means obtained from any set of observations, as at the end of Table 2, the high-frequency deflections of the instruments under test corresponding to the low-frequency deflections, for equal current in the standard instrument, are obtained. The results may be plotted as performance curves, or they give at once $\frac{I_a}{(I_a)_0}$, the ratio of the current indicated at high frequency to the current indicated at low frequency or direct current, with the same total current in the circuit. Suppose the instrument under test is one composed of several wires in parallel with a thermocouple on the wire *a*. Suppose

TABLE 2

Frequency	Two-wire standard	"Unshunted" ammeter	Seven-wire ammeter
	398.6	+0.03	−0.03
2700	461.2	6.48	6.15
	460.5	6.49	6.14
	460.0	6.43	6.10
		6.45	6.15
	Mean 460.6	6.46	6.14
750 000	459.4	6.58	8.85
	457.7	6.60	8.80
	457.2	6.50	8.80
		6.58	8.75
		6.50	
	Mean 458.4	6.55	8.80
2700	460.9	6.48	6.15
	460.3	6.49	6.14
	460.3	6.46	6.15
	460.0	6.49	6.15
	460.2	6.48	6.18
	Mean 460.3	6.48	6.15
750 000	458.0	6.41	8.80
	457.0	6.55	8.75
	457.0	6.52	8.75
	457.3	6.53	8.70
		6.55	8.80
	Mean 457.3	6.51	8.76
2700	460.3	6.48	6.18
	459.8	6.52	6.18
	459.8	6.48	6.18
		6.50	6.20
		6.50	6.19
		6.57	
	Mean 459.9	6.50	6.19
	399.0	+0.05	−0.01
Mean 2700	460.27	6.48	6.16
Mean 750 000	457.85	6.53	8.78

that the per cent change, k, of current in the wire a can be calculated for any desired frequency from the inductances, etc., as in Section III below. Then, using I_a for the current in the wire a, and I for the whole current in the circuit, and the subscript $_o$ to denote direct-current or low-frequency values, the theoretically predicted relation is

$$\frac{I_a}{I} = \frac{(I_a)_o}{(I)_o}(1 + k)$$

For the same total current on high frequency as on low frequency, i. e., for $I = (I)_o$,

$$\frac{I_a}{(I_a)_o} = 1 + k \qquad (2)$$

Now, coming to the experimental performance of the instrument, the indicating device is such that

$$\text{Indicated } I = \text{constant} \times I_a \qquad (3)$$

or,

$$\frac{\text{Indicated } I}{(\text{Indicated } I)_o} = \frac{I_a}{(I_a)_o},$$

which, by equation (2), $= 1 + k$. That is,

$$\frac{\text{Indicated } I - (\text{Indicated } I)_o}{(\text{Indicated } I)_o} = k \qquad (4)$$

Computation from the experimental results is made according to equation (4), thus obtaining by experiment a quantity also theoretically calculable. This reasoning is subject to the limitation that equation (3) may not be exactly fulfilled when the current distribution changes and the wires are not all at the same temperature. Thus the wire in which the current is measured may be influenced by convection and radiation from its neighbors; this will always tend to equalize the temperatures and reduce the apparent change of current distribution. The effect of convection is more variable when the measurement is made thermoelectrically, being determined by the temperature at a single point, than in other methods, such as the expansion of the wire, in which the temperature throughout the length of the wire is integrated. Calculation of the change of indicated current with frequency, as made according to equation (4), is such as to insure correct relationships of the curves at different frequencies, independent of temporary changes of calibration such as might arise, e. g., from temperature change. Thus, the direct-current calibration points before and after high-frequency observations may not lie exactly on the same curve; but the change of calibration does not affect interpretation of the curves, for the high-frequency points are plotted at the correct distances from the direct-current curve as drawn. The relation of indicated high-frequency current to the actual current flowing is not the important thing, but rather the relation of indicated high-frequency current to indicated direct-current or low-frequency current for equal total current in the circuit.

4. SOURCES OF ERROR

(a) ACCIDENTAL ERRORS

The precision of an observation in general was 0.5 per cent of the current measured, and the precision of a mean of several observations was about 0.2 per cent or 0.3 per cent. The chief source of accidental error was the lack of constancy of the high-frequency current, together with the different lag constants of the two galvanometers. In the strip instruments described later, the thermal lag of the strips themselves was appreciable, and in one case was greater than the mechanical lag of the galvanometer used on the standard instrument. A necessary precaution in the observations was to shield each galvanometer by connecting one of its binding posts to its case. Before this was done, irregular leakage of direct currents from lighting circuits was the cause of peculiar and puzzling results. A few possible sources of constant error in the observations will now be treated.

(b) EDDY CURRENTS

It has been suspected that eddy currents in neighboring conductors might affect the readings of hot-wire ammeters. This was investigated by greatly exaggerating the conditions that might occur in practice. A copper sheet 2 mm thick and about 6 cm square was placed very close to one of the wires of the two-wire standard instrument, which was in series with two other instruments. At a frequency of 750 000, the presence of the sheet made no perceptible difference in the currents indicated. The same thing was tried with an iron sheet with the same result. The absence of eddy current effect upon high-frequency ammeters is also confirmed by the experience of a commercial manufacturer of instruments;[7] the confidence of the company in respect to this point being so great that they inclose their best high-frequency ammeter in an iron case.

(c) INDUCTIVE EFFECT OF LEADS, ETC.

It is very reasonable to suppose that outside parts of a circuit, particularly the leads, might inductively affect an ammeter at high frequency. The effect of distant portions of the circuit was tested by changing the orientation of instruments by 180°, and also by moving the instruments into different positions at distances 15 to 80 cm from the secondary circuit inductance coil. No changes in reading were noticeable. It was otherwise with the leads, however. In the cases tried, the readings were not affected by the presence of the leads when extending straight out from the binding posts to some distance, as they would usually be connected. But when a lead was turned and run along the side of an instrument which consisted of more than a single wire, there were appreciable changes. These were very evidently due to the greater mutual inductance of the lead upon the parts of the ammeter circuit nearest to it than upon the more remote parts. The changes were of the algebraic sign and of a magnitude to be expected from experience with the effects described in later sections of this paper. For example, with a frequency of 1 000 000, upon placing the lead wire in the plane of and parallel to the three-wire instrument of Fig. 9 below, about 5 cm distant from the three wires, as shown in Fig. 6, the current in the wire *a′* decreased 1.5 per cent. Upon reversing the direction of the lead, the current in the same wire increased 1.5 per cent. This effect

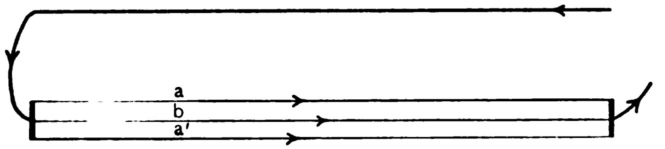

Fig. 6.—*Experiment upon proximity of lead wire*

could be strikingly illustrated[8] by replacing the three-wire system of Fig. 6 by a vacuum tube; the high-frequency current would *visibly* crowd to the side of tube nearest the lead when the lead was directed as in Fig. 6, and vice versa. Similar results were obtained with the instrument of Fig. 19 below. With the lead adjacent and parallel to the long, thick copper wire ST of this instrument, 4 cm distant from it, with the current in the two opposed, the current in the right section of the instrument increased 3 per cent at a frequency of 500 000. These effects are large enough to suggest the need for caution in any radiotelegraphic circuit, particularly when the ammeter is very close to other parts of the circuit.

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[7] R. Hartmann-Kempf: Elektrotech. Zs., 32, p. 1134; 1911. G. Eichhorn: Jahrbuch d. Drahtl. Tel., 5, p. 517; 1912.

(d) LOW FREQUENCY

The results of experiments throughout this investigation were found not to depend on the low frequency with which the high-frequency effects were compared. Frequencies of 60, of 550, and of 2700 cycles were used, and all gave consistent results. Any frequency of this order is practically equivalent to zero frequency or direct current, in these experiments, because the changes of current distribution in the instruments here used only begin at frequencies of the order of 100 000.

(e) CAPACITY

Electrostatic capacity was found to affect the experiments at the highest frequency used, 1 500 000, but at no lower frequency. The effect was serious, causing two ammeters in series to carry different amounts of current; but, as will be shown, a way was found to eliminate it. There was no indication that the capacity of the high-frequency circuit itself affected matters. The observed result was found to be due rather to the relatively large capacity of the measuring galvanometers and leads, used in the thermocouple circuits of the instruments. This effect was at first very puzzling. Two instruments whose readings agreed at all lower frequencies showed an unaccountable difference of 5 per cent in the current indicated at 1 500 000. This difference was consistently maintained until one day the difference was found to have changed very suddenly from + 5 per cent to − 5 per cent.

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[8] J. J. Thomson: "Recent Researches," p. 511; 1893.

This was surprising, and the source of trouble was sought by altering various connections of different parts of the circuit. It was found that the effect changed sign when the leads a and b to the two instruments X and N, in Fig. 7, were interchanged. That the difference was due to an actual difference in the current flowing in the two instruments was suggested by the fact that if the observer touched the case of one of the galvanometers, a continuous spark passed, and the deflections of the galvanometers changed, even though the person stood on insulating blocks. The existence of a capacity current to the ground was thus manifested. The effects were further studied, exaggerating them by connecting a wire from a metal pipe lying on the floor to various parts of the instruments and their circuit. Current left the circuit and flowed along this wire, changing the deflections of the instruments by amounts depending on where the connection was made. This indicated strongly that the observed errors were due to part of the current leaving the circuit from some point between the two instruments, and as the instruments and their attached galvanometers were well insulated by hard rubber blocks it appeared to be a capacity current.

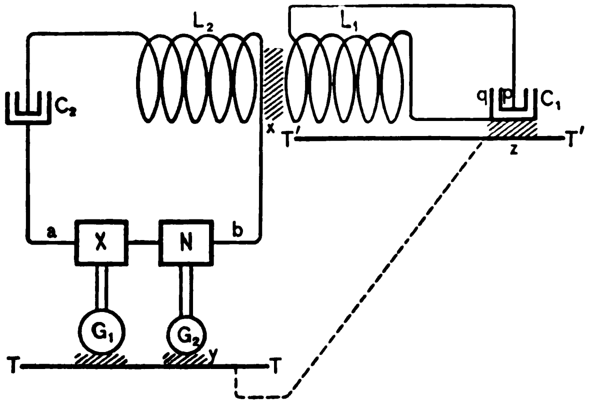

Fig. 7.—*Diagram showing path of dielectric current*

The effect is explained by electrostatic induction of current across the adjacent ends of the primary and secondary inductance coils. The electrostatic circuit is completed through the instruments and galvanometers, thence as a dielectric current to the wooden table T T, thence partly as dielectric and partly conduction current to the slate table T′ T′, and thence as a dielectric current to the outer coating of the Leyden jar C_1. The capacity in the circuit thus completed simply acts as a condenser in parallel with the Leyden jar. This is made clearer by Fig. 8, which is equivalent to those portions of Fig. 7 concerned in this phenomenon. The instantaneous current electrostatically induced seemed to be opposite in direction to that electromagnetically induced in the secondary circuit, so as to reduce the whole current flowing in the instruments. The current in the instrument to which the lead b (Fig. 7) was connected was less than the current in the other instrument, because part of this dielectric current left the circuit through the galvanometer of the former and so never reached the latter. The theory was corroborated by interchanging the connections of the coil L_2 in Fig. 7. Then the current was less in the instrument to which the lead a was connected, as expected.

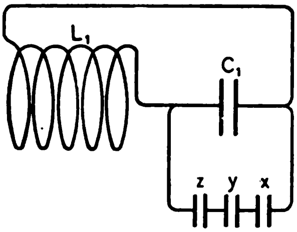

Fig. 8.—*Theoretical equivalent of Fig. 7*

If this explanation were valid, it was thought that it might be possible to eliminate the effects, for the purposes of ammeter comparison, by shunting the dielectric current around the ammeters in some way. It is only required that the currents in the two instruments be the same, regardless of the current in other parts of the circuit. It was successfully accomplished by connecting a wire from the lead b (Fig. 7) to a metal plate under the primary Leyden jar C_1, the jar standing upon hard-rubber blocks on the plate. This provided a path of much lower impedance than through the ammeters and tables. When this device was used, the current through the two ammeters was the same, within the limits of observational error, as shown by interchanging the leads a and b. These results were obtained repeatedly with a number of different pairs of instruments. The success of this scheme to shunt the dielectric current out of the ammeters is strong evidence for the explanation postulated for the observed effects. If the trouble had been caused by the distributed capacity of the ammeter wires themselves, then neither this scheme nor any other could make the current in the two ammeters equal.

The magnitude of the observed effects is found to be consistent with calculation. The amounts of current flowing in the Leyden jar and in the complex dielectric path are proportional to the capacities of the paths. Since the current in the complex dielectric path was found by observation to be 5 per cent of the total secondary current, assuming the primary current roughly to be the same as the secondary, the capacities must be in the ratio 20 to 1. Since the capacity of the Leyden jar C_1 was 1500 micromicrofarads, the capacity of the complex dielectric path was therefore about 75 micromicrofarads. This is an exceedingly small capacity; and is a not unreasonable value for the circuit considered, even though the three capacities x, y, and z are in series. It may be recalled, for comparison, that the capacity of an isolated sphere equals its radius in centimeters, and that 1 micromicrofarad = 0.9 cm. The dimensions of the parts here concerned are smaller than 75 cm, but on the other hand they are by no means isolated. The reasons why the capacity effects were not appreciable at the lower frequencies were: (a) That the primary and secondary coils were separated a greater distance, and hence the capacity was smaller; and (b) that the current in the primary circuit was relatively smaller, for there was visible brush discharge from the primary Leyden jar at 1 500 000 and in no other case.

The capacity effect which has been investigated appears to have a decided bearing upon many experiments at radiotelegraphic frequencies. Similar leakage of current from primary[9] to secondary circuits is familiar in practical work. It can be eliminated for the purposes of certain kinds of measurements, as shown above.

III. THE PARALLEL WIRE AMMETER

The first type of ammeter circuit which suggests itself for carrying a large high-frequency current is a group of several fine wires in parallel. This has been used by a number of experimenters and instrument makers, but it does not appear that its limitations have been distinctly pointed out. As shown below, it is in some cases subject to most serious errors. The most important source of error is mutual inductance between the wires, which has usually been thought negligible. The readings of the instrument depend on the current in just one of the wires. It will be shown that changes in the distribution of current among the wires affect such an instrument to a much greater percentage amount than the percentage change of resistance of the system as a whole.

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[9] Electrician, 68, pp. 1017, 1063; 1912.

1. ILLUSTRATIVE THREE-WIRE INSTRUMENT

Let us consider a simple case, which illustrates the essential features of this type of instrument. Three copper wires, each 10 cm long and 0.08 mm in diameter, were placed parallel, 4.0 mm apart, all in one plane. They were soldered at the ends to conductors whose resistance or impedance could be neglected. The leads were connected to the ends of this system at right angles to its plane, and other parts of the circuit were some distance away. The current distribution in such a system can be calculated for any frequency and can also be experimentally measured by the methods described in Section II. A hard-soldered copper Eureka thermocouple was used, which could be soft-soldered to any wire.

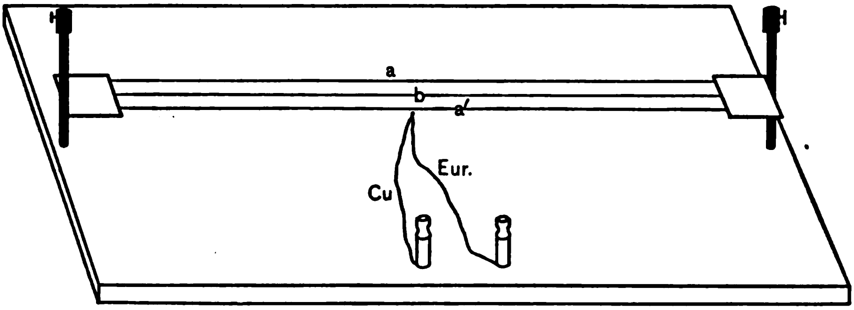

Fig. 9.—*Instrument of three parallel wires*

Let R_a, R_b, $R_{a'}$ = resistance of a, b, a', respectively,

L = self-inductance of any one wire,

M_{ab}, $M_{aa'}$ = mutual inductances,

l = length of wire = 10.0 cm,

δ = diameter of wire = 0.008 cm,

d = distance between wires = 0.4 cm.

If a direct current be passed through the system, each wire carries one-third of the whole current, provided the wires all have exactly the same resistance. If, however, a current of high frequency be passed through the system, the two outer wires each carry more than one-third of the current and the middle wire less than one-third. This may be understood in a qualitative way from the well-known tendency of a high-frequency current to crowd toward the outer portions of a conductor as the frequency is raised. It is obtained quantitatively by considering the impedances of the system.

In the first place, the wires are so fine that the current distribution within the individual wire is not altered. The self and mutual inductances of the wires, neglecting bending of the current at the ends, may be calculated by well-known expressions,[10] and by the mode of connection assumed, no inductive action of other parts of the circuit need be considered. The frequencies dealt with are not so great but that for these small circuits the magnetic field may be considered as established instantaneously. The self-inductance of a single straight wire is given by the expression:

$$L = 2l\left(\log \frac{4l}{\delta} - 0.75\right) \tag{5}$$

For wires of such small diameter the high-frequency and low-frequency inductance are not appreciably different. The mutual inductance of two parallel wires when δ is small and l is large in comparison with d,

$$M = 2l\left(\log \frac{2l}{d} - 1 + \frac{d}{l}\right) \tag{6}$$

In the present case we find:

$$L = 20\ .\ (8.51 - 0.75) = 155.\ \text{cm}$$
$$M_{ab} = M_{a'b} = 20\ .\ (3.91 - 0.96) = 59.\ \text{cm}$$
$$M_{aa'} = 20\ .\ (3.22 - 0.92) = 46.\ \text{cm}$$

The calculations may be most easily understood by first considering frequencies so great that the resistance is small in comparison with the reactance. Expressions for the current distribution will be obtained by neglecting the resistance. Calling e the electromotive force between the two ends of the system, and i_a, i_b, respectively, the instantaneous currents in a and b, and I_a, I_b the effective values of current,

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[10] Rosa and Grover: This Bulletin, 8, pp. 150, 174; 1911.

$$e = L\frac{di_a}{dt} + M_{ab}\frac{di_b}{dt} + M_{aa'}\frac{di_a}{dt}$$

$$= L\frac{di_b}{dt} + 2M_{ab}\frac{di_a}{dt} \qquad (7)$$

It is obvious that $i_a = i_{a'}$ since $M_{ab} = M_{a'b}$.
Integrating (7), there results at once:

$$(L + M_{aa'})I_a + M_{ab}I_b = LI_b + 2M_{ab}I_a \qquad (8)$$

or,

$$(L + M_{aa'} - 2M_{ab})I_a = (L - M_{ab})I_b \qquad (9)$$

$$\frac{I_a}{I_b} = \frac{L - M_{ab}}{L + M_{aa'} - 2M_{ab}} = \frac{155. - 59.}{155. + 46. - 118.} = 1.155$$

Denoting by I the whole current flowing,

$$I = 2I_a + I_b, \text{ or } 2 + \frac{I_b}{I_a} = \frac{I}{I_a}$$

Now, for very low frequencies or direct current, which will be denoted by the subscript $_o$, $\frac{(I_a)_o}{(I_b)_o} = \frac{R_b}{R_a}$, and $2(I_a)_o + (I_b)_o = (I)_o$, so that

$$2 + \frac{R_a}{R_b} = \frac{(I)_o}{(I_a)_o} \qquad (10)$$

For $I = (I)_o$, i. e., the same total current in the circuit, $\frac{I_a}{(I_a)_o} = \frac{2 + \frac{R_a}{R_b}}{2 + \frac{I_b}{I_a}}$. If $R_a = R_b$, this ratio becomes $\frac{I_a}{(I_a)_o} = \frac{3}{2 + \frac{I_b}{I_a}}$, the numerical magnitude of which here $= 1.047$.
Similarly,

$$\frac{I_b}{(I_b)_o} = \frac{1 + 2\frac{R_b}{R_a}}{1 + 2\frac{I_a}{I_b}}$$

the numerical magnitude of which here $= 0.906$.

These are the limiting values of the currents for very high frequencies, i. e., for any frequency so high that the resistances are negligible in comparison with the reactances. It is shown below, both experimentally and theoretically, that this condition is pretty closely approached at a frequency of 1 500 000. If the temperature of one of the wires be measured by a thermocouple or expansion indicator or other thermometric device, the current indicated on low frequency would be exactly one-third the whole current flowing if the resistances of all three wires were exactly equal; and at any frequency higher than 1 500 000 or so the current indicated would be 9.4 per cent lower if the middle wire be used and 4.7 per cent higher if either outside wire be used.

For a system consisting of two parallel wires instead of three, a consideration of equations similar to (7) above and (11) below shows at once that each carries the same current at all frequencies, provided the two wires are exactly similar. The advantages and limitations of a two-wire system have been treated in Section II.

The current distribution in the three-wire system will now be calculated for frequencies such that the resistance can not be neglected. The potential difference between the ends is:

$$\begin{aligned} e &= R_a i_a + L\frac{di_a}{dt} + M_{ab}\frac{di_b}{dt} + M_{aa'}\frac{di_{a'}}{dt} \\ &= R_b i_b + L\frac{di_b}{dt} + M_{ab}\frac{di_a}{dt} + M_{ab}\frac{di_{a'}}{dt} \end{aligned} \qquad (11)$$

By symmetry, $i_{a'} = i_a$, if $R_a = R_{a'}$; in any case understand by i_a the mean instantaneous current in a and a', and by R_a the mean resistance of a and a'. Since at every instant, $2i_a + i_b =$ the total instantaneous current, i,

$$i_b = i - 2i_a \qquad (12)$$

Substitute in (11),

$$\begin{aligned} R_a i_a + (L + M_{aa'} - 2M_{ab})\frac{di_a}{dt} = R_b i - 2R_b i_a + (L - M_{ab})\frac{di}{dt} \\ - 2(L - M_{ab})\frac{di_a}{dt} \end{aligned}$$

Assuming that e is harmonic, and solving,[11]

$$[(R_a+2R_b)^2+p^2(3L+M_{aa'}-4M_{ab})^2]I_a^2=[R_b^2+p^2(L-M_{ab})^2]I^2 \quad (13)$$

in which $p=2\pi \times$ frequency. Similarly, solving for I_b^2,

$$\begin{aligned}[(R_a+2R_b)^2+p^2(3L+M_{aa'}-4M_{ab})^2]I_b^2 \\ =[R_a^2+p^2(L+M_{aa'}-2M_{ab})^2]I^2\end{aligned} \quad (14)$$

By equation (10),

$$\frac{I_a}{(I_a)_o}=\sqrt{\frac{I_a^2}{I^2}}\left(2+\frac{R_a}{R_b}\right) \quad (15)$$

Similarly,

$$\frac{I_b}{(I_b)_o}=\sqrt{\frac{I_b^2}{I^2}}\left(1+\frac{2R_b}{R_a}\right) \quad (16)$$

The quantities under the radical sign in (15) and (16) are given in (13) and (14), respectively.

The significance of these solutions is made clearer by considering special cases. If the frequency is very low, equation (13) reduces to (10). If the resistances were equal, the current in one wire would be precisely one-third the whole current flowing, just as was shown above. In the instrument constructed to test these calculations, however, the resistances were not exactly equal. Copper wires of such small diameter vary greatly in cross section and hardness. By actual measurement the resistance of the wire b was found to be 0.352 ohm, and the mean resistance of a and a' was 0.347 ohm. The difference of cross section corresponding to

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[11] Rewrite the differential equation:

$$(R_a+2R_b)i_a+(3L+M_{aa'}-4M_{ab})\frac{di_a}{dt}=(R_b)i+(L-M_{ab})\frac{di}{dt}.$$

Assuming e harmonic, it can be expressed in the ordinary way as proportional to $\epsilon^{\sqrt{-1}\,pt}$, where ϵ is the Napierian base, p is 2π times the frequency, and t is time. Letting I_a and I represent effective values of current, and a and β angles of phase difference,

$$i_a=I_a\epsilon^{\sqrt{-1}\,pt}\epsilon^{\sqrt{-1}\,a}$$

$$i=I\epsilon^{\sqrt{-1}\,pt}\epsilon^{\sqrt{-1}\,\beta}$$

Substituting in the differential equation,

$$\begin{aligned}(R_a+2R_b)I_a\epsilon^{\sqrt{-1}\,pt}\epsilon^{\sqrt{-1}\,a}+\sqrt{-1}\,p(3L+M_{aa'}-4M_{ab})I_a\epsilon^{\sqrt{-1}\,pt}\epsilon^{\sqrt{-1}\,a} \\ =R_bI\epsilon^{\sqrt{-1}\,pt}\epsilon^{\sqrt{-1}\,\beta}+\sqrt{-1}\,p(L-M_{ab})I\epsilon^{\sqrt{-1}\,pt}\epsilon^{\sqrt{-1}\,\beta}\end{aligned}$$

Simplifying,

$$[(R_a+2R_b)+\sqrt{-1}\,p(3L+M_{aa'}-4M_{ab})]I_a\epsilon^{\sqrt{-1}\,a}=[R_b+\sqrt{-1}\,p(L-M_{ab})]I\epsilon^{\sqrt{-1}\,\beta}$$

Taking absolute values of these complex quantities, since the absoulte value of $\epsilon^{\sqrt{-1}\,a}$ and of $\epsilon^{\sqrt{-1}\,\beta}$ equals 1,

$$[(R_a+2R_b)^2+p^2(3L+M_{aa'}-4M_{ab})^2]I_a^2=[R_b^2+p^2(L-M_{ab})^2]I^2$$

Thus equation (13) has been derived.

this difference of reisistance causes no appreciable difference in the self-inductances,

$$\frac{(I_a)_o}{(I)_o}=\frac{0.352}{0.347+0.704}=0.334_0, \text{ instead of exactly } 0.3333$$

$$\frac{(I_b)_o}{(I)_o}=\frac{0.347}{0.347+0.704}=0.330_2, \text{ instead of exactly } 0.3333$$

If the frequency is extremely high the resistance terms can be neglected in (13) and (14), giving

$$\frac{I_a}{I_b}=\frac{L-M_{ab}}{L+M_{aa'}-2M_{ab}},$$

the same as equation (9) above, which was independently deduced.

For any frequency whatever, substituting numerical values in (13) and (15), and letting f = frequency,

$$\frac{I_a}{(I_a)_o}=\sqrt{\frac{0.124+0.364(10)^{-12}f^2}{1.105+2.98\ (10)^{-12}f^2}}[2.986] \qquad (17)$$

Similarly,

$$\frac{I_b}{(I_b)_o}=\sqrt{\frac{0.120+0.272(10)^{-12}f^2}{1.105+2.98\ (10)^{-12}f^2}}[3.029] \qquad (18)$$

Values have been calculated from these expressions for four frequencies, and compared with the experimental observations. The results follow:

TABLE 3

Current Distribution in Three-Wire System

Frequency	Per cent increase of current in *a*		Per cent decrease of current in *b*	
	Calculated	Observed	Calculeted.	Observed
	Per cent	Per cent	Per cent	Per cent
150 000	0.3	0.4	0.6	0.2
500 000	1.8	1.3	3.4	3.0
1 000 000	3.1	2.8	6.1	5.3
1 500 000	3.9	3.6	7.4	6.0
∞	4.3	....	8.5	....

The agreement of the observed values with the calculations is nearly as good as the experimental accuracy warrants. It should have been expected, however, that the observed values would be numerically smaller than the calculated values, because of the heat interchange among the three wires due to convection and radiation. The thermocouple method of observation measures primarily the *temperature* of one of the wires, from which the current in the wire is *inferred*. When the three wires are carrying different amounts of current their temperatures are to a certain extent equalized by the interchange of heat, and hence the wires will appear to be carrying currents more nearly equal than they actually are. This conclusion was corroborated by observations on an instrument similar to the one considered except that the wires were 2 mm instead of 4 mm apart. On account of the wires being closer together, the effect of heat interchange should be more marked and the per cent changes of current should be still smaller than the calculated values. Such was found to be the case, and, furthermore, the changes were not constant, but different on different days; apparently the amount of convection varied with different temperature or atmospheric conditions. Contrary to expectation, the results were not improved by placing this instrument in a partial vacuum under a pressure of 1 cm of mercury.

Table 3 shows that at a frequency of 1 500 000 the current distribution has become nearly that for infinite frequency. Of course, "infinite" must be understood simply as meaning such a frequency that the resistance is a negligible part of the impedance. For mathematically infinite frequency the current distribution is indeterminate. For any frequency higher than 1 500 000 there are practically no further changes, except that the resistance of the individual wires becomes appreciably greater; the ratio of currents, however, remains practically unchanged. Thus the remarkable fact becomes evident that the range of frequencies investigated, in which all the changes in current distribution take place, is just the range of frequencies utilized in radiotelegraphy.

2. INSTRUMENT OF SEVEN WIRES

A hot-wire ammeter employing a more complex type of parallel wire resistance was examined and tested with high-frequency currents. It was a commercial instrument with the ordinary arrangements for indicating expansion. The resistance consisted of seven bronze wires, each 8.6 cm long and 0.15 mm in diameter, spaced as shown in Fig. 10, six of them being 0.19 cm apart and the seventh, *g*, being at a distance of 0.95 cm from *f*. The flexible leads to *g*, each about 0.3 mm diameter, will be called *m* and *m′*. The indicating mechanism of the ammeter is a device for showing the expansion of the wire *g*. 9 amperes gave full-scale deflection. It will readily be seen that because of the mutual inductances the wire *g* will carry more current than any of the other wires when the frequency is high, while with direct current it will carry approximately the same as any other wire (actually a trifle less than one of the others because of the resistance of *m* and *m′*). Consequently the instrument will "read high" on high frequency. As shown below by calculation and by experiment, this effect is surprisingly large. The complete theoretical solution for all frequencies can not be obtained for such a complex case, but enough can be worked out to explain the instrument's behavior.

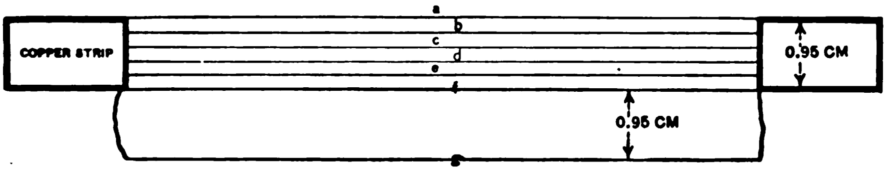

Fig. 10.—*Instrument of seven parallel wires*

The inductances, calculated by (1) and (2) above and by a more accurate expression for mutual inductance in the cases of the wires farther apart, are as follows:

$$
\begin{aligned}
L_a &= \ldots\ldots\ldots L_f = 120.2 \text{ cm} \\
L_g &= L_a + 2L_m \quad = 158.8 \\
M_{ab} &= M_{bc} = \ \ldots = \ 60.7 \\
M_{ac} &= M_{bd} = \ \ldots = \ 49.2 \\
M_{ad} &= M_{be} = \ \ldots = \ 42.6 \\
M_{ae} &= M_{bf} = 38.0 \\
M_{af} &= M_{fg} = 34.6 \\
M_{eg} &= 31.7 \\
M_{dg} &= 29.5 \\
M_{cg} &= 27.4 \\
M_{bg} &= 25.7 \\
M_{ag} &= 24.3
\end{aligned}
$$

For frequencies so high that the resistance is negligible compared with the reactance, the condition that the potential difference be the same between the ends of each branch of the system, assuming harmonic electromotive force, is—

$$\begin{aligned}
&L_aI_a+M_{ab}I_b+M_{ac}I_c+M_{ad}I_d+M_{ae}I_e+M_{af}I_f+M_{ag}I_g\\
&=M_{ab}I_a+L_bI_b+M_{ab}I_c+M_{ac}I_d+M_{ad}I_e+M_{ae}I_f+M_{bg}I_g\\
&=M_{ac}I_a+M_{ab}I_b+L_cI_c+M_{ab}I_d+M_{ac}I_e+M_{ad}I_f+M_{cg}I_g\\
&=M_{ad}I_a+M_{ac}I_b+M_{ab}I_c+L_dI_d+M_{ab}I_e+M_{ac}I_f+M_{dg}I_g\\
&=M_{ae}I_a+M_{ad}I_b+M_{ac}I_c+M_{ab}I_d+L_eI_e+M_{ab}I_f+M_{eg}I_g\\
&=M_{af}I_a+M_{ae}I_b+M_{ad}I_c+M_{ac}I_d+M_{ab}I_e+L_fI_f+M_{fg}I_g\\
&=M_{ag}I_a+M_{bg}I_b+M_{cg}I_c+M_{dg}I_d+M_{eg}I_e+M_{fg}I_f+L_gI_g
\end{aligned}$$

Inserting numerical values:

$$\begin{aligned}
&120.2I_a+60.7I_b+49.2I_c+42.6I_d+38.0I_e+34.6I_f+24.3I_g\\
&=60.7I_a+120.2I_b+60.7I_c+49.2I_d+42.6I_e+38.0I_f+25.7I_g\\
&=49.2I_a+60.7I_b+120.2I_c+60.7I_d+49.2I_e+42.6I_f+27.4I_g\\
&=42.6I_a+49.2I_b+60.7I_c+120.2I_d+60.7I_e+49.2I_f+29.5I_g\\
&=38.0I_a+42.6I_b+49.2I_c+60.7I_d+120.2I_e+60.7I_f+31.7I_g\\
&=34.6I_a+38.0I_b+42.6I_c+49.2I_d+60.7I_e+120.2I_f+34.6I_g\\
&=24.3I_a+25.7I_b+27.4I_c+29.5I_d+31.7I_e+34.6I_f+158.8I_g
\end{aligned}$$

Combining the last line with each of the preceding, these equations become the first six of the following:

$$\begin{aligned}
0&=95.9I_a+35.0I_b+21.8I_c+13.1I_d+6.3I_e+0-134.5I_g\\
0&=36.4I_a+94.5I_b+33.3I_c+19.7I_d+10.9I_e+3.4I_f-133.1I_g\\
0&=24.9I_a+35.0I_b+92.8I_c+31.2I_d+17.5I_e+8.0I_f-131.4I_g\\
0&=18.3I_a+23.5I_b+33.3I_c+90.7I_d+29.0I_e+14.6I_f-129.3I_g\\
0&=13.7I_a+16.9I_b+21.8I_c+31.2I_d+88.5I_e+26.1I_f-127.1I_g\\
0&=10.3I_a+12.3I_b+15.2I_c+19.7I_d+29.0I_e+85.6I_f-124.2I_g\\
I&=I_a+I_b+I_c+I_d+I_e+I_f+I_g
\end{aligned}$$

The last equation expresses the obvious condition that the currents are all in the same phase when the resistance is negligible (I denotes the whole current in the circuit).

Solving these equations by the use of determinants, we find:

$$\frac{I_g}{I}=0.196$$

On low frequency, however, the ratio of the current in the wire g to the total current is determined solely by the resistances. The resistance of the instrument was found to be 0.027 ohm, and the resistance of the wire g, measured after severing its leads, was 0.213.

$$\therefore \frac{(I_g)_0}{(I)_0} = \frac{0.027}{0.213} = 0.127$$

For a given total current in the circuit, the ratio of the current in the wire g at an extremely high frequency to the current in g at low frequency is then

$$\frac{I_g}{(I_g)_0} = \frac{0.196}{0.127} = 1.55$$

That is, for a frequency so high that the resistance is a negligible part of the impedance, the instrument would read 55 per cent high.

The behavior of the instrument at any frequency whatever may be calculated approximately by the aid of assumptions. The wire g is so unsymmetrically situated that to a first approximation the variations among the currents in the other six wires may be neglected. Suppose each of the wires a to f replaced by a wire occupying the position s (Fig. 11). Let the mutual inductances of each of these six wires at s with respect to the other five be the same as the average mutual inductances when the wires occupy their positions a to f; i. e., the mutual inductances of one wire at s with respect to the others are taken to be approximately the same as the mutual inductances of the wire b with respect to a, c, d, e, and f. Let ΣM_s denote the sum of these five mutual inductances. The mutual inductances of the wires at s with respect to g are all the same, M_{gs}. The potential difference between the ends of any wire is:

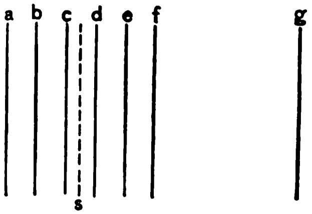

Fig. 11.—*Diagram for approximate calculation of seven-wire instrument*

$$e = R_s i_s + (L_s + \Sigma M_s)\frac{di_s}{dt} + M_{gs}\frac{di_g}{dt}$$

$$= R_g i_g + L_g \frac{di_g}{dt} + 6M_{gs}\frac{di_s}{dt}$$

Now, $i = 6i_s + i_g$. $\therefore i_s = \frac{i - i_g}{6}$. Substitute this value for i_s.

$$\frac{R_s}{6} i + \left(\frac{L_s + \Sigma M_s}{6} - M_{gs}\right)\frac{di}{dt} = \left(R_g + \frac{R_s}{6}\right) i_g$$
$$+ \left(L_g + \frac{L_s + \Sigma M_s}{6} - 2M_{gs}\right)\frac{di_g}{dt}$$

Solving as in footnote 11, letting p denote 2π times the frequency,

$$\left(\frac{I_g}{I}\right)^2 = \frac{\left(\frac{R_s}{6}\right)^2 + p^2\left(\frac{L_s + \Sigma M_s}{6} - M_{gs}\right)^2}{\left(R_g + \frac{R_s}{6}\right)^2 + p^2\left(L_g + \frac{L_s + \Sigma M_s}{6} - 2M_{gs}\right)^2}$$

Inserting numerical values, $\Sigma M_s = 251.2$ cm, and letting f denote the frequency:

$$\frac{I_g}{I} = \sqrt{\frac{0.00096 + 0.0439(10)^{-12}f^2}{0.0594 + 1.056(10)^{-12}f^2}}$$

This quantity divided by the value of $\frac{(I_g)_0}{(I)_0}$ gives the ratio of the indicated current at a frequency f to the indicated current at very low frequency. Thus for a frequency of 100 000,

$$\frac{I_g}{(I_g)_0} = \frac{0.141}{0.127} = 1.11$$

and for a frequency of 750 000,

$$\frac{I_g}{(I_g)_0} = \frac{0.198}{0.127} = 1.56$$

Therefore the ammeter should read 11 per cent high at a frequency of 100 000, and 56 per cent high at 750 000.

The actual performance of the instrument is shown by the curves of Fig. 12. The readings obtained at various frequencies are there plotted against the current. Throughout the scale, the readings at the different frequencies differ by approximately a constant per cent, as expected. At 100 000 the readings are 10 per cent high, and at 750 000 they are 46 per cent high. Measurements could not be made at higher frequencies than 750 000, because the instrument did not have a sufficiently open scale for observations below 6 amperes and currents as great as that could not be maintained steady enough at higher frequencies. The agreement between performance and theoretical calculation is quite satisfactory in view of the roughly approximate character of the assumptions made in the calculation of the preceding paragraph. Furthermore, the spacing of the wires *a* to *f* in Fig. 11 is not quite uniform, and the wire *a* is partly shunted by a wire three times its diameter (for purposes of adjustment). Heat interchange by convection and radiation, which would reduce the observed changes of reading, may be appreciable, although it is much less than it would be if the wire *g* were closer to the other wires. This thermal effect would make the changes appear less for larger currents, and the observations indicated this; but the relatively lower precision of the observations with smaller currents made it impossible to correct for the effect.

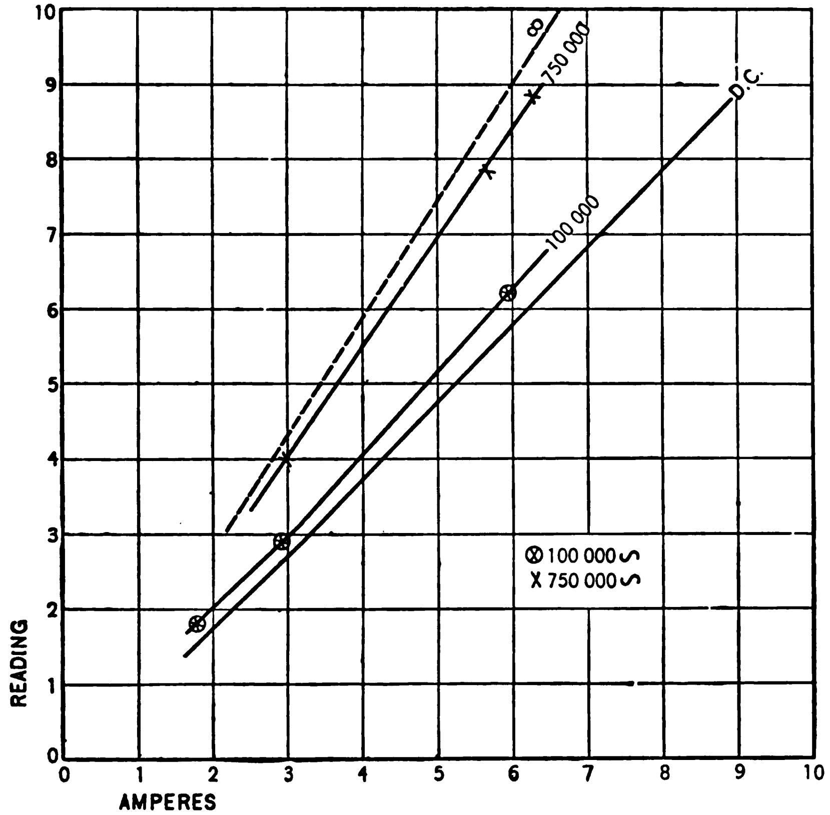

Fig. 12.—*Effect of frequency, seven-wire instrument*

3. USE OF HIGH-RESISTANCE WIRES

The changes in current distribution at a given frequency can be much reduced by using wires of higher resistance. This was proved, experimentally and theoretically, in the case of the three-wire instrument of Fig. 9. An exactly similar instrument was constructed, the copper wires of 0.08 mm diameter being replaced by Eureka wires of 0.05 mm diameter. The resistivity of Eureka is about thirty times that of copper, and consideration of equations (17) and (18) of page 117 shows that the change of current in any wire, up to a frequency of 1 500 000, should be zero. Measurement gave the following results:

TABLE 4

Frequency	150 000	500 000	1 000 000	1 500 000
Decrease of current in *b*	−0.5 per cent	+0.4 per cent	−0.2 per cent	−0.1 per cent

The first two results were each a single observation; the departure of all the values from zero may be considered error of observation.

Thus the changes of current distribution can be moved up, as it were, to frequencies higher than those used in radiotelegraphy by employing wires of high resistance. The distribution of currents at a frequency so great that the resistance is a small part of the impedance is in nowise altered; that condition simply holds at a higher frequency. Even a wire of resistivity intermediate between that of copper and the high-resistance materials, such as platinum (resistivity 6.4 times copper), makes the changes of distribution negligible up to a frequency of 1 500 000, in the case of this particular type of instrument. The caution must be given, however, that the diameter of the wire should not be increased, as then the advantage of the higher resistivity of the wire disappears. This caution is necessary because instrumental requirements work against high resistance, for it increases the heat production, and the large heat production is the problem in constructing an ammeter for large currents; and again the designer will surely be tempted to use larger diameters when he substitutes higher resistivity wires for copper because he knows that the skin effect, or change of resistance with frequency of the wire itself, is less as the resistivity increases.

This advantage of using high-resistance metal for the working resistance holds as well for the flat-strip type of ammeter treated in Section V as for the parallel-wire type. The advantage is not quite so great, however, in the second class of instruments, the so-called unshunted type, as will be brought out in Section IV.

4. AMMETERS OF PREVIOUS EXPERIMENTERS

An ammeter of the parallel-wire type, used by H. W. Edwards [12] in investigating high-frequency resistance, has some points of interest. It consisted of 15 wires in parallel between two triangular blocks of copper with a thermocouple soldered to the center wire. The wires were 3 cm long, 2 mm apart, and 0.08 mm in diameter. It is found by calculation that the self-inductance of one wire is 39. cm, and the 14 mutual inductances range from 11. to 3. cm. Comparison with the cases calculated above shows that for frequencies high enough to make the reactances comparable with the resistances, the instrument would read a good many per cent lower than on direct current. The change of distribution in the massive copper terminal blocks would increase the error. The latter effect is appreciable, as shown by the experiments on strip instruments in Section V; and, in fact, is

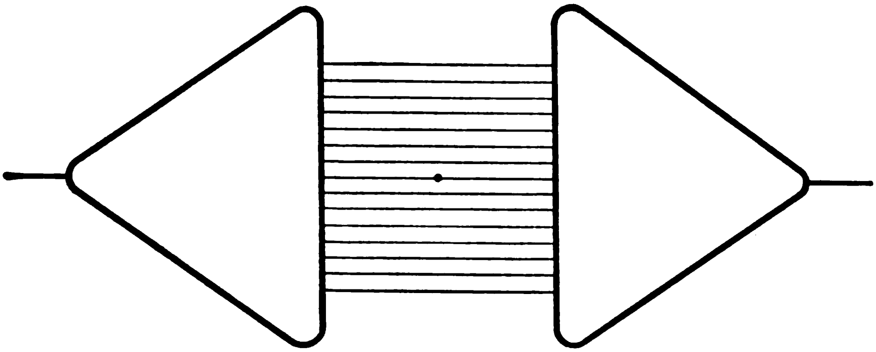

Fig. 13.—*Edwards' parallel-wire ammeter*

probably the only effect that would manifest itself at radiotelegraphic frequencies, as the wires were of high-resistance material. As Edwards' experiments were made at frequencies below 300 000, the instrument probably caused no error in his work.

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[12] Phys. Rev., 33, p. 184; 1911.

A form of construction recommended by Fleming, and also described by A. H. Taylor,[13] is subject to still another error. It is shown in Fig. 14, and is simply a group of parallel wires between a pair of posts. Supposing that the wires could be spaced so far apart that the mutual inductances would have negligible effect, there would still be high-frequency errors if the self-inductances of all parts were not in the ratio of their resistances. The posts are of relatively large cross section, and their resistance is quite negligible in comparison with the resistance of the wires, but the self-inductance of the posts may be of the same order of magnitude as the self-inductance of the wires. Then the high-frequency current in wire *z* will be much less than in wire *u*. This effect has been observed experimentally by Edwards (loc. cit.), the upper wire being found to carry 30 per cent less current than the lower at a frequency of 300 000. This effect is also illustrated experimentally in Section IV, following, in the present paper. In the ammeter constructed by Taylor the wires were of high-resistivity metal, but were of a relatively large diameter, 0.16 mm, so that the change of current distribution might be appreciable at radiotelegraphic frequencies.

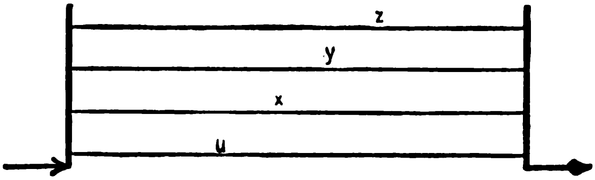

Fig. 14.—*Parallel-wire ammeter of various experimenters*

The error would not be removed from this instrument by connecting the current leads at the middle points of the posts, for then the self-inductance in the paths of I_u and I_z would be greater than in the paths of I_x and I_y. This effect would decrease the current in the outside wires, while the mutual inductances would increase it. However, if the leads be connected at opposite corners, at right angles to the plane of the instrument, as in Fig. 15, the self-inductance in each current path will be the same, and furthermore the leads will have no inductive action upon the instrument. If the leads were connected at opposite corners, as prolongations of the posts instead of at right angles to the posts, conditions would be almost as good; but each lead would act inductively on the adjacent section of the post somewhat more than on the other sections, and hence the middle sections of the post would carry somewhat more current than the end sections. This same principle is utilized in an instrument which employs thin, flat strips instead of wires, described in section V.

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[13] Phys. Rev., **34**, p. 365; 1912.

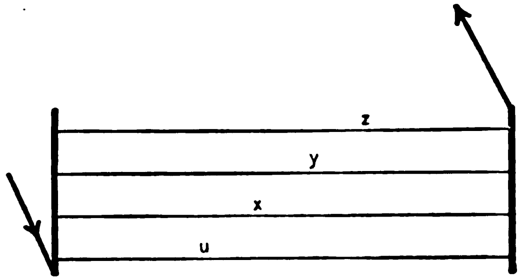

Fig. 15.—*Improved method of lead connection*

5. CYLINDRICAL ARRANGEMENT

The errors of the parallel-wire type of ammeter, due to mutual and self inductance, can be avoided by arranging the wires as equidistant elements of a cylinder and leading the current in to the centers of the ends of the cylinder. The mutual inductances of each wire with respect to the others are the same, and the self inductance is the same in each current path. The currents in the different wires must then be the same, at high frequencies. The current can be measured by a thermocouple or an expansion device on one of the wires. It turns out that this is so good a

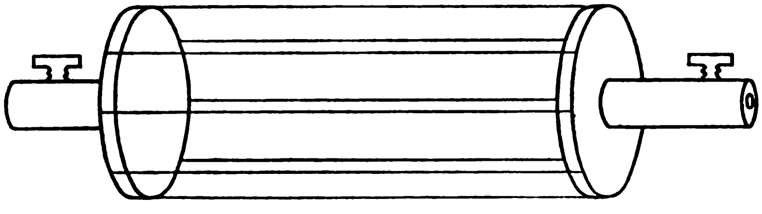

Fig. 16.—*Parallel-wire ammeter of cylindrical design*

high-frequency instrument that its only errors are due to its low-frequency current distribution. Great care is necessary to make sure that the wires all have the same resistance, otherwise they carry different amounts of current at low frequencies. In such an instrument, actually constructed of 8 manganin wires, 0.24 mm diameter and 6 cm long, the mechanicians found it difficult to solder on the wires without stretching and heating them unequally and consequently the resistances were not near enough to equality. Measurements showed that the increase of current in one of the wires from direct current was +4.8 per cent at 1 000 000, in another was 0.0 per cent, and in another −4.3 per cent. (These measurements were obtained by soldering the thermocouple successively on the three wires. Observations at other frequencies were consistent with those stated.) The greatest care in selection of wire and in construction is necessary to insure the equality of the resistances of the fine wires which must be used. This understood, the instrument may be a valuable one. The cylindrical arrangement of wires was first realized by Broca, and was described by him in Bulletin de la Société Internationale des Électriciens, **9**, p. 423; 1909. The symmetrical arrangement has also been utilized by R. Hartmann-Kempf [14], in the construction of instruments which employ thin metal strips instead of wires, described below in section V.

6. UTILIZATION OF WHOLE HEAT PRODUCTION

A way of escape from the current distribution errors of the parallel-wire type of ammeter is to make the deflection depend on the whole heat production in the system instead of on that in one branch. Now the whole heat production does change with change of frequency, because the resistance of the system considered as a whole increases as the current departs more and more from uniform distribution; but, as will be shown in the next section, the change of resistance of the whole system is of a smaller order of magnitude than the change of current distribution. In many cases, therefore, an instrument which is seriously in error if its reading depends on the current in one branch would have negligible error if it were so arranged that its readings depended on the whole current. The calorimetric instrument, in which the reading depends for example on an air-thermometer device, avoids the direct errors of current distribution. The same thing holds for the expansion-indicating instrument of the so-called unshunted type, treated in the next section, but it will be there shown that in those particular instruments the dissymmetry of current distribution is likely to be so enormous that the change of resistance of the whole is not negligible. Another form of expansion-indicating instrument which avoids the direct errors of current distribution has been reported to the author. A number of wires parallel to one another were mechanically connected in such a way that the expansion of all of them contributed to the deflection. It so happened that the wires were less than 1 mm apart, so that the mutual inductances were large, and the change of current distribution was very great. Upon trial with high frequency currents the instrument was found to read high. The reading of any ammeter which depends on the whole heat production, or whole current through it, will either increase with frequency or will remain practically unchanged, but can not decrease.

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[14] See footnote 7, p. 107.

This principle is readily applied to the instruments which employ a thermocouple as the means of indication. It was tried out in the three-wire case discussed first in the present section. Three thermocouples in series were used, one on each wire, the direction of connection being alternately reversed. The resultant emf of such a series should be an average about equal to that of one couple. The construction was very simple, as shown in Fig. 17, a fine copper wire lead being soldered to the middle point of *a*, and at the same point a fine Eureka wire (shown dotted) which went to *b*, then a copper wire to *a′*, and finally a Eureka lead; the two leads of course connect to a galvanometer. Theoretical calculation made as shown below, in the next section,

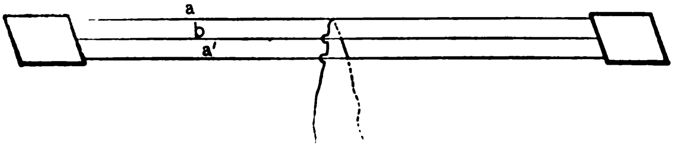

Fig. 17.—*Three-thermocouple instrument*

shows that the change of reading should be negligible at all frequencies up to 1 500 000. Measurements at 500 000, 1 000 000, and 1 500 000 confirmed this; the increase of reading at 1 500 000 being 0.4 per cent, which was within the error of observation.

7. SUMMARY

Summarizing the investigation of the parallel-wire type of ammeter, it has been found that large errors with high-frequency currents occur in commonly used instruments, these errors being chiefly due to the mutual inductances and in some cases to self-inductances which had been thought negligible. These errors can be avoided for frequencies in the range employed in radiotelegraphy by using wires of high resistance. In some instruments in which the errors are due to the self-inductances of connecting parts they can be eliminated by suitable location of the current leads. Still another method of avoiding error is symmetrical location of the wires, such that each has the same mutual inductances with respect to the others. The errors are much reduced and in some cases eliminated entirely by making the deflection depend on the whole heat production instead of on the current in only part of the working resistance; this is possible in general for instruments whose deflections are produced either by calorimetric effect, expansion, or thermolectric effect.

IV. THE SO-CALLED UNSHUNTED AMMETER

Probably the type of ammeter most widely used in the past in radiotelegraphic work is that which employs but a single hot wire with different portions of its length joined in parallel. It will be shown that some of these have serious errors while others have not, and that the errors can be lessened. The construction is most readily understood from the diagram, Fig. 18. A and B are the current leads. They connect to thick copper bars, from which flexible metal strips take the current to several points of the hot wire, whose expansion is measured by the ordinary device (not shown in Fig. 18). Thus a single wire carries the whole current, and the instrument is therefore called unshunted. The resistances of the copper bar and metal strips are negligible in comparison with the resistance of the hot wire, and if the lengths of the sections in parallel are the same each carries the same current as any other on low frequency. But the inductances of these parts are by no means negligible, and consequently on high frequency the different portions of the wire carry different amounts of current. In fact, in practical cases the impedance of the hot wire itself is but a small part of the impedance of each current path for high frequencies. Even the mutual inductances of the different portions of the "hot wire" are not negligible and in themselves tend to cause more current to flow in the central sections than in the outer sections. (This is rather unusual, as high-frequency currents tend to go to the outer portions of a conductor in general, but note that the direction of current is here reversed in adjacent sections). The changes in current distribution from the uniformity of direct-current distribution are in fact very large. They are equivalent to an increase in the resistance of the system as a whole, so that these instruments tend to read high on high frequency. It will be shown that the location of the leads A and B has an important influence in determining the error; and that some instruments of this type could be greatly improved by changing these points of connection.

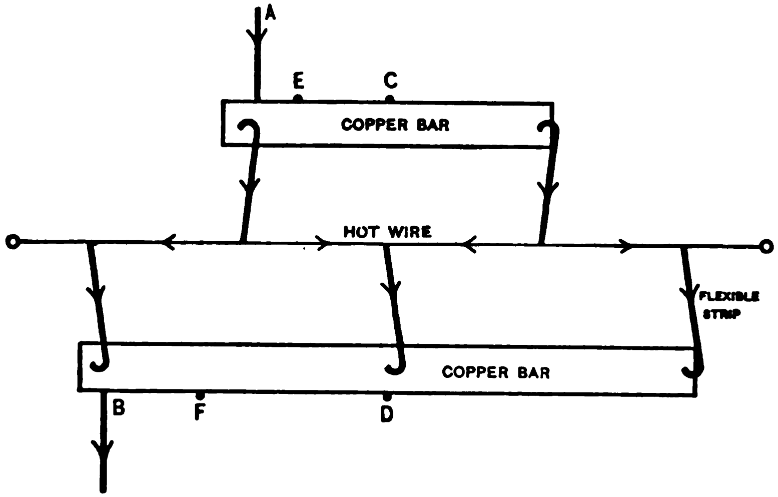

Fig. 18.—*Unshunted ammeter of four sections*

1. ILLUSTRATIVE INSTRUMENT OF TWO SECTIONS

The actual distribution of current was studied, both experimentally and theoretically, in the case of a typical instrument of two sections. P O Q is a fine copper wire, 0.08 mm in diameter, soldered at the ends to the ends of P S T Q, which is a thick copper wire, 2.6 mm in diameter, bent at right angles in the two points S and T. This device exactly simulates the "unshunted" type of ammeter, P O Q being the "hot wire." Current leads were connected, perpendicular to the plane of this system, at the corner S and at O, the middle point of the fine wire. A thermocouple was soldered to some point on either P O or O Q, and its leads attached to a galvanometer; the deflection of the galvanometer was then a measure of the current flowing in P O or O Q. The length P O = O Q = 4.9 cm, and the length P S = T Q = 2.0 cm. For convenience in considering the current in the two branches of the system the diagram is redrawn, Fig. 20. The lengths P O and O Q, of Fig. 19, are here denoted by *b* and *c*, which have resistances R_1 and R_2, respectively. It could not be taken for certain that these two resistances were equal, although the lengths were equal, because such very thin copper wires are not uniform in diameter or in hardness. By measurement it was found that $R_1 = 0.168$ ohm and $R_2 = 0.179$ ohm.

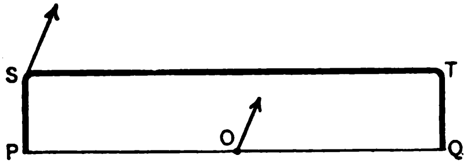

Fig. 19.—*Instrument with two sections of hot wire in parallel*

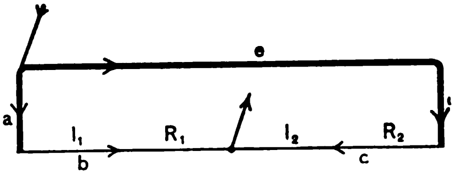

Fig. 20.—*Paths of current in two-section instrument*

For direct current or alternating current of low frequency R_1 and R_2 are the whole impedances of the two current paths, the resistance of the thick copper wire being quite negligible. But for high frequencies the inductances of these latter portions affect the impedance to an important extent. At very high frequencies, in fact, all resistances are negligible; and the self-inductance of e is actually greater than that of c; and, furthermore, the mutual inductances between e and b, between e and c, and between b and c appreciably affect the current distribution. No inductive action of outside portions of the circuit need be considered, as the leads are brought in at right angles to the wires of the system and other portions of the circuit are some distance away.

The self-inductances of b and c may be calculated by the simple expression:

$$L=2l\left(\log\frac{4l}{\delta}-0.75\right).$$

But the inductances of the thick wire portions, L_a, L_d, and L_e, are not the same on high as on low frequency because of change of current distribution in the thick wire itself. Thus for low frequencies the self-inductance of e is found by the simple calculation to be 75.0 cm, while for the high frequencies used in the experiments below it is found (see footnote 4) to be 71.0 cm. The mutual inductance of two parallel wires of length l and $\frac{1}{2}l$ and d cm apart, situated as e and b in Fig. 20, is readily shown to be:

$$M_{be}=l\log\frac{l+\sqrt{l^2+d^2}}{d}-\sqrt{l^2+d^2}+d. \qquad (19)$$

The mutual inductance of two adjacent wires in the same straight line, each of length l, such as b and c, is:

$$M_{bc}=1.386l. \qquad (20)$$

The numerical values of the high-frequency inductances are found to be:

$L_b=L_c=69.0$ cm
$L_a=L_d=10.0$
$L_e=71.0$
$M_{bc}=6.8$
$M_{be}=M_{ce}=12.7$

In the actual instrument constructed the current lead was not attached exactly at the corner S, but 1 cm to the right of the corner. The slight alteration of L_e and departure from equality of M_{be} and M_{ce} produce negligible effects in the results.

The current distribution at any frequency may be calculated as follows. The potential difference between the ends of either wire is:

$$e = R_1 i_1 + (L_a + L_b)\frac{di_1}{dt} + (M_{be} - M_{bc})\frac{di_2}{dt}$$

$$= R_2 i_2 + (L_c + L_d + L_e)\frac{di_2}{dt} - 2M_{ce}\frac{di_2}{dt} + (M_{be} - M_{bc})\frac{di_1}{dt}$$

Since $L_c = L_b$, $L_d = L_a$, and $M_{ce} = M_{be}$,

$$R_1 i_1 + (L_a + L_b + M_{bc} - M_{be})\frac{di_1}{dt} = R_2 i_2$$

$$+ (L_a + L_b + L_e + M_{bc} - 3M_{be})\frac{di_2}{dt}$$

At every instant, $i_1 + i_2 = i$, the total instantaneous current, or, $i_2 = i - i_1$

$$\therefore\ (R_1 + R_2)i_1 + (2L_a + 2L_b + L_e + 2M_{bc} - 4M_{be})\frac{di_1}{dt}$$

$$= R_2 i + (L_a + L_b + L_e + M_{bc} - 3M_{be})\frac{di}{dt}$$

Assuming that e is harmonic and solving as in footnote 11,

$$\frac{I_1^2}{I^2} = \frac{R_2^2 + p^2(L_a + L_b + L_e + M_{bc} - 3M_{be})^2}{(R_1 + R_2)^2 + p^2(2L_a + 2L_b + L_e + 2M_{bc} - 4M_{be})^2}$$

For very low frequencies, which are denoted by the subscript $_0$,

$$\frac{(I)_0}{(I_1)_0} = 1 + \frac{(I_2)_0}{(I_1)_0} = 1 + \frac{R_1}{R_2},\ \text{or}$$

$$\therefore\ \frac{I_1}{(I_1)_0}\,\frac{(I)_0}{I} = \frac{I_1}{I}\left(1 + \frac{R_1}{R_2}\right)$$

For a given total current in the circuit, i. e., $(I)_0 = I$,

$$\frac{I_1}{(I_1)_0} = \sqrt{\frac{R_2^2 + 4\pi^2 f^2(L_a + L_b + L_e + M_{bc} - 3M_{be})^2}{(R_1 + R_2)^2 + 4\pi^2 f^2(2L_a + 2L_b + L_e + 2M_{bc} - 4M_{be})^2}}\left[1 + \frac{R_1}{R_2}\right]$$

f denoting the frequency.

Inserting numerical values,

$$\frac{I_1}{(I_1)_0} = \sqrt{\frac{0.0320 + 0.556(10)^{-12} f^2}{0.120\ \ + 1.45\ (10)^{-12} f^2}}\,[1.939] \qquad (21)$$

Similarly, for branch 2 of the instrument, it may be shown that the ratio of the indicated current at a frequency f to the indicated current at very low frequency is:

$$\frac{I_2}{(I_2)_0}=\sqrt{\frac{0.0282+0.211(10)^{-13}f^2}{0.120\ +1.45\ (10)^{-13}f^2}}[2.065] \qquad (22)$$

A correction was applied to these calculations to take account of the fact that the current heated the copper wires, so that their resistance while working was not the same as when measured cold.

For the range of frequencies in which changes in the current ratios occur, measurements were obtained and are compared with the values calculated from (21) and (22) in the following table:

TABLE 5

Current Distribution in "Unshunted" System

Frequency	Per cent increase of current in 1		Per cent decrease of current in 2	
	Calculated	Observed	Calculated	Observed
	Per cent	Per cent	Per cent	Per cent
150 000	4.5	4.2	4.2	4.4
500 000	15.2	14.3	15.4	15.0
1 000 000	18.6	17.7	19.4	18.7
1 500 000	19.2	19.1	20.3	19.5
∞	20.0	....	21.1	....

Of course, as before, "infinite" frequency simply means such a frequency that the resistance is a negligible part of the impedance. These results are also presented graphically in Fig. 21, in which the continuous curves give theoretical values and the dots inclosed by circles represent the observations.

The asymptotic approach of the current ratios to the values for infinite frequency is particularly well shown by these curves. Physically infinite frequency is practically attained. The agreement of the observations with the theory is all that could have been expected. There is no error here, however, due to heat interchange between the working parts, as in the case of the parallel wire instruments. The two parts of the hot wire were purposely made long and were soldered at their junction *O* (Fig. 19), to a heavy metal post to reduce their thermal effect upon each other. It was found, too, that the results obtained did not differ appreciably whether the thermocouple was soldered to the middle of one of the wires or close to its outer end.

The slight discrepancy between the theory and experiment is to be attributed to the insufficiency of the inductance calculations. In calculating the inductance of a finite portion of a circuit it is

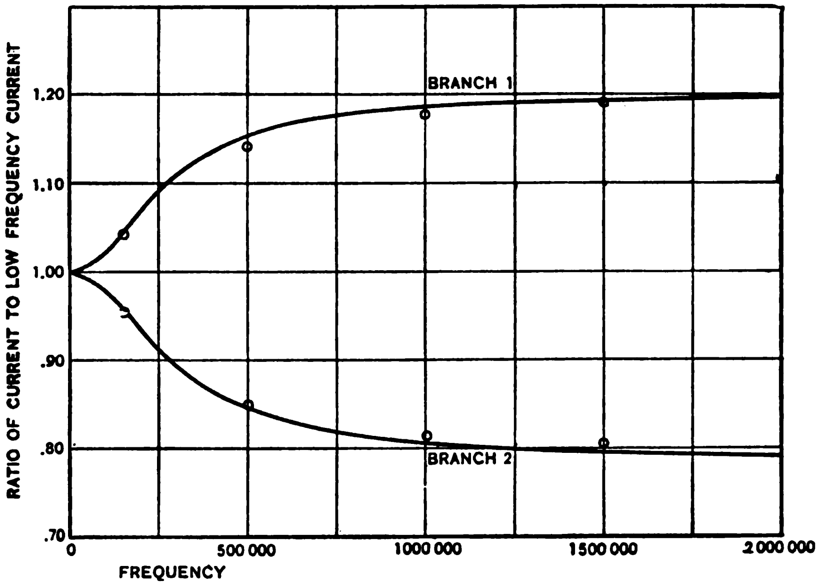

Fig. 21.—*Change of current distribution with frequency, two-section instrument*

assumed that the current is uniformly distributed about the axis of the conductor. This does not hold near a bend in the conductor; and furthermore the inductance of the current at the bend is neglected. Hence, one could not be sure how accurately the inductances of short lengths, such as those of the present case, are obtained by the theoretical formulas. The present experimental results are themselves a justification of the use of those formulas for approximate calculation even of such short lengths. Independent justification of the simple formulas for inductances of short linear conductors, in a somewhat more favorable case, is furnished by the direct inductance measurement [15] of Grover and Curtis.

The instrument under discussion not only illustrates the error in the "unshunted" type of instrument, but also the error treated in Section III in connection with Fig. 14. It is there brought out that while the resistance of the posts is negligible, the self-inductance is very important. The thick copper wire in the instrument here experimented upon plays the same part as the posts in Fig. 14, and hence the error there discussed is here experimentally realized.

2. USE OF HIGH-RESISTANCE WIRES

If the two-section instrument of Fig. 19 had a hot wire of some material of higher resistivity than copper, the changes of current distribution would be decreased. This is evident from a consideration of equations (21) and (22), pages 134, 135. It was proved experimentally by making a reproduction of the instrument, replacing the copper wire of 0.08 mm diameter by a Eureka wire of 0.05 mm diameter. The resistivity of Eureka wire is about thirty times that of copper, and calculation shows that up to a frequency of 1 500 000 the change of current distribution should be zero. The mean experimental results, for the ratio of high-frequency current to low-frequency current in the right section, were:

TABLE 6

Frequency	150 000	500 000	1 000 000	1 500 000
Per cent decrease of current	Per cent 0.0	Per cent 0.3	Per cent 0.2	Per cent 0.2

The difference between these results and zero is within the experimental error.

If, however, the instrument were made of a material of some intermediate resistivity, such as platinum or bronze, the changes of current distribution would be decidedly appreciable. In fact, if it were made of such material and the wires were of larger diameter than the copper wires (as they might be, since the skin effect is less as the resistivity increases), the errors might be fully as great as when the hot wire is of copper. This will be illustrated in experiments to follow. There is not so great an advantage in using high-resistance metal in the hot wire of the "unshunted" type as in the parallel wire type of Section III because here the impedance of the hot wire itself plays a smaller part in determining the high-frequency current distribution.

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[15] This Bulletin, 8, p. 468, Reprint 175; 1911.

3. INSTRUMENT OF FOUR SECTIONS

A commercial "unshunted" instrument of the four-section type sketched in Fig. 18 (p. 131) was considered and tested with high-frequency currents. The "hot wire" is of platinum 0.3 mm diameter and the working portion is 10. cm in length, so that the length of each section, *a*, *b*, *c*, *d* (Fig. 22) is 2.5 cm; 10 amperes give full scale deflection. The current has four paths in the instrument, which makes a system too complex for complete theoretical solution at all frequencies. However, the current distribution can be calculated for frequencies so great that the resistance is a negligible portion of the impedance, which will enable interpretation of the experimental results.

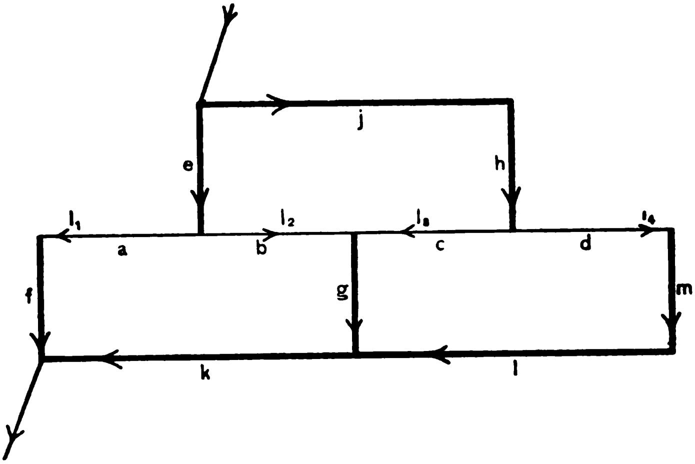

Fig. 22.—*Paths of current in four-section instrument*

The two leads, shown at the extreme left corners, did not enter precisely at the corners; the effect of this will be considered later.

In the calculation it is necessary to take account of the self-inductance of each part, as well as the mutal inductances between parts, as follows, M_{ab}, M_{kl}, M_{jb}, M_{ka}, and the other equal mutual inductances of similarly situated parts. We may neglect the smaller mutual inductances M_{eh}, M_{fm}, M_{ac}, M_{ad}, M_{jk}, M_{kc}, and the similar mutual inductances equal to these. For frequencies so high that the resistance is negligible compared with the reactance, the condition that the potential difference be the same between the ends of each branch of the system is:

$$\begin{aligned}
&L_e(I_1+I_2)+\underline{L_aI_1}+L_fI_1-M_{ab}I_2+M_{ka}(I_2+I_3+I_4)\\
&=L_e(I_1+I_2)+\underline{L_bI_2}+L_g(I_2+I_3)+L_k(I_2+I_3+I_4)+M_{jb}(I_3+I_4)\\
&\qquad -M_{ab}I_1-M_{bc}I_3-M_{kb}(I_2+I_3+I_4)+M_{ka}I_1-M_{kb}I_2+M_{kl}I_4\\
&=L_j(I_3+I_4)+L_h(I_3+I_4)+\underline{L_cI_3}+L_g(I_2+I_3)+L_k(I_2+I_3+I_4)+M_{jb}I_2\\
&\qquad -M_{jc}I_3-M_{jc}(I_3+I_4)-M_{bc}I_2-M_{cd}I_4+M_{lc}I_4+M_{ka}I.\\
&\qquad -M_{kb}I_2+M_{kl}I_4\\
&=L_j(I_3+I_4)+L_h(I_3+I_4)+\underline{L_dI_4}+L_mI_4+L_lI_4+L_k(I_2+I_3+I_4)\\
&\qquad +M_{jb}I_2-M_{jc}I_3-M_{cd}I_3-2M_{ld}I_4+M_{lc}I_3+M_{kl}(I_2+I_3+I_4)\\
&\qquad +M_{kl}I_4+M_{ka}I_1-M_{kb}I_2
\end{aligned}$$

The four terms underlined in these equations are the only ones that might be taken into account, at first thought, in the consideration of the high-frequency behavior of this kind of instrument. As a matter of fact, these terms are quite small compared to others in the equations, as may be seen from the following numerical values of the inductances.

Many of the inductances in the equations are equal to one another, so that there are only six different ones. They may be calculated by (5), (19), (20), above, and the following formula for the self-inductance of a straight conductor of rectangular cross section, having width $=\alpha$ and thickness $=\beta$:

$$L=2l\left[\log\frac{2l}{\alpha+\beta}+0.5+\frac{0.2235(\alpha+\beta)}{l}\right] \qquad (22)$$

This gives the low frequency inductance, but comparison with the calculation (p. 133) for a round wire shows that the high-frequency value will be only slightly different. The calculation is only approximate anyway, for the bending of the current around corners is neglected. The six inductances were found to be:

$$
\begin{aligned}
L_e &= 43.7 \text{ cm}\\
L_a &= 25.3\\
L_k &= 33.5\\
M_{ab} &= 3.5\\
M_{kl} &= 6.9\\
M_{ka} &= 3.6
\end{aligned}
$$

Inserting the numerical values, and adding an equation to express the summation of currents, there results:

$$
\begin{aligned}
109.1I_1 + 3.4I_2 - 110.5I_3 - 216.2I_4 &= 0\\
40.2I_1 + 98.6I_2 - 40.4I_3 - 179.4I_4 &= 0\\
0 + 33.3I_2 + 58.4I_3 - 105.7I_4 &= 0\\
I_1 + I_2 + I_3 + I_4 &= I
\end{aligned}
$$

Solving for the currents in the four sections:

$$
\begin{aligned}
I_1 &= 0.495I\\
I_2 &= 0.158I\\
I_3 &= 0.190I\\
I_4 &= 0.156I
\end{aligned}
$$

(The sum of the four coefficients is 0.999, a sufficient check upon the computations). The dissymmetry of the current distribution is surprisingly great.

We come now to the essential characteristic of this type of instrument. The currents in all four sections affect the deflection, so that there will not be the enormous changes of deflection which would be expected if the current in just one section were measured. The error of the instrument is appreciable, nevertheless. It is well known that the direct current distribution of currents in any system is that of minimum heat production, so that the change of distribution with increase of frequency means an increase of total heat production. As the deflections of these instruments depend on the total heat production, they will read high on high frequency. The increase of total heat production for a given total current is equivalent to an increase in the resistance of the instrument; and it will be seen from the following that this change in resistance is of a smaller order of magnitude than the change in current distribution.

Consider a system of any n conductors in parallel between two points of a circuit, all of the same resistance and of such cross sections that the resistance of each individually is not appreciably different on high and low frequency.

Let R_k = resistance of any single branch of system,
R = high-frequency resistance of whole system,
$(R)_o$ = direct-current or low-frequency resistance of whole system,
n = number of branches of system,
I_k = high-frequency current in one branch,
$(I_k)_o$ = direct current or low-frequency current in one branch,
I = whole high-frequency current in circuit,
$(I)_o$ = whole direct current or low-frequency current in circuit,
H = rate of total heat production by high-frequency current,
$(H)_o$ = rate of total heat production by direct current or low-frequency current.

Since the resistances of all the branches are the same,

$$(R)_o = \frac{R_k}{n}$$

$$(I)_o = n(I_k)_o$$

$$(H)_o = \sum_{k=1}^{k=n} R_k (I_k)_o^2 \tag{23}$$

$$= n[R_k (I_k)_o^2] = n\left[n(R)_o \frac{(I)_o^2}{n^2}\right]$$

Or,

$$(H)_o = (R)_o (I)_o^2 \tag{24}$$

Similarly to (23), for high frequencies,

$$H = \sum_{k=1}^{k=n} R_k I_k^2$$

Or,

$$H = n(R)_o \sum_{k=1}^{k=n} I_k^2 \tag{25}$$

Similarly to (24), we can write:

$$H = RI^2, \tag{26}$$

this equation defining R, the high-frequency resistance of the system as a whole. For a given total current, by (24) and (26),

$$\frac{H}{(H)_0}=\frac{R}{(R)_0}, \tag{27}$$

or, obviously, the total rate of heat production is proportional to the resistance of the whole system, for a given current in the circuit.

We have, by (24) and (25),

$$\frac{H}{(H)_0}=\frac{n}{(I)_0^2}\sum_{k=1}^{k=n} I_k^2,$$

or, for the same total current on high frequency as on low, setting $I^2=(I)_0^2$, we have:

$$\frac{H}{(H)_0}=\frac{n}{I^2}\sum_{k=1}^{k=n} I_k^2 \tag{28}$$

In a hot-wire ammeter the scale and the mechanism for indicating the expansion are such as to satisfy the following relation:

$$\text{Indicated } I=\text{constant}\times\sqrt{H} \tag{29}$$

$$\therefore \frac{\text{Indicated } I \text{ for high frequency}}{\text{Indicated } I \text{ for low frequency}}=\sqrt{\frac{H}{(H)_0}} \tag{30}$$

Returning to the four-section ammeter under consideration, we have calculated above the numerical values of $\frac{I_k}{I}$ for each of the four sections. Inserting them in (28),

$$\frac{H}{(H)_0}=4.[(0.495)^2+(0.158)^2+(0.190)^2+(0.156)^2]=1.322$$

By (30), the ratio of the indicated currents $=\sqrt{1.322}=1.15$; i. e., the instrument should read 15 per cent high at a frequency so great that the resistance is a negligible portion of the impedance.

The foregoing calculations were repeated on the assumption that the leads of the instrument were connected at the middle of the two copper bars at the points C and D, Fig. 18, instead of at the points A and B as shown. The result of the calculation is that the change of reading would be negligible at all frequencies. The instrument would not read so much as 0.1 per cent high at "infinite" frequency. This result will appear reasonable upon inspection of Fig. 18 and consideration of the impedances in each current path. Hence, the location of the leads is of very great importance.

In the instrument tested the leads actually were attached at the points E and F, situated about two-thirds of the distance

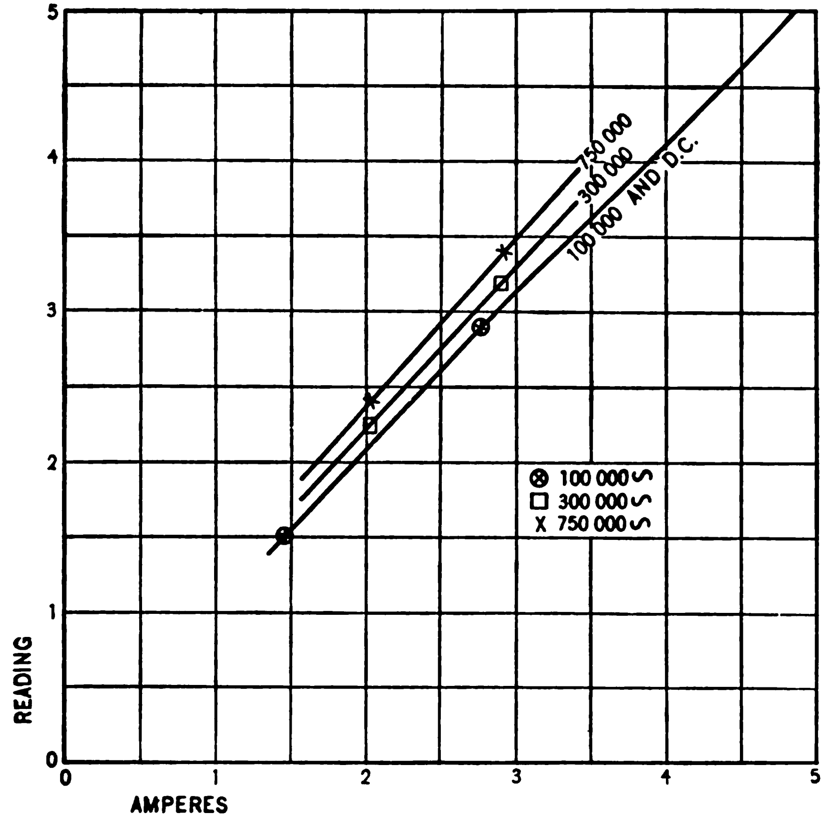

Fig. 23.—*Effect of frequency, four-section ammeter*

C A from C and two-thirds D B from D. The error of the instrument is certainly intermediate between the two cases already calculated, and we may roughly assume it to be two-thirds that calculated when the leads are connected at the corners. It should therefore read two-thirds of 15 per cent high at "infinite" frequency, i. e., 10 per cent high. The readings which the instrument gave experimentally are plotted in Fig. 23. The readings are found from the curves to be 11.5 per cent high at a frequency of 750 000, and 6 per cent high at 300 000, and at 100 000 to be the same as on direct current.

A consideration of the resistances and inductances and a comparison with the calculations for the two-section instrument above indicate that the current distribution at a frequency of 750 000 is here practically the same as at "infinite" frequency. (The resistance of each of the four sections was 0.04 ohm.) The agreement between the theoretical value of 10 per cent for "infinite" frequency and the observed value of 11.5 per cent for 750 000 is quite satisfactory. There is some possible question as to whether the expansion of the hot wire for a given total heat production will be the same, when the distribution of heat along it is uniform, and when more heat is produced in some sections than others; this is the question of the validity of equation (29). Any error due to this cause will probably be small and will be reduced an unknown amount by heat conduction along the wire.

4. ADDITIONAL COMMERCIAL INSTRUMENTS

Although it has been shown that an instrument of the type under consideration can be improved by symmetrical location of the current leads, it does not always follow that such instruments can thus be entirely freed from error. This is shown in the case of a six-section instrument represented in diagram in Fig. 24. The hot wire A B is about 10 cm.long. The heavy lines indicate copper bars, which are connected to the hot wire by flexible

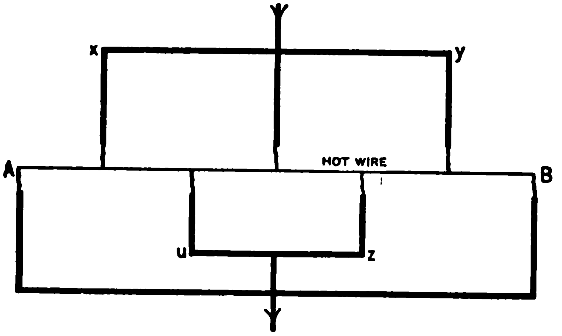

Fig. 24.—"Unshunted" ammeter of six sections

wires. As indicated, the current enters and leaves at center points of the connecting bars. However, inspection of the diagram suggests that there are differences of current distribution because the inductances of the several current paths differ materially. It was found by a calculation similar to that made for the four-section instrument above that this instrument should read 8 per cent high at a frequency so great that the resistances are negligible portions of the impedances. The results of actual measurement at 750 000 are plotted in Fig. 25, from which the increase of reading is found to be 3 per cent. It was not to be expected that the resistances would be negligible at 750 000, because the hot wire was of a high-resistance material. Nevertheless, the wire was relatively thick, having a diameter of 0.3 mm,

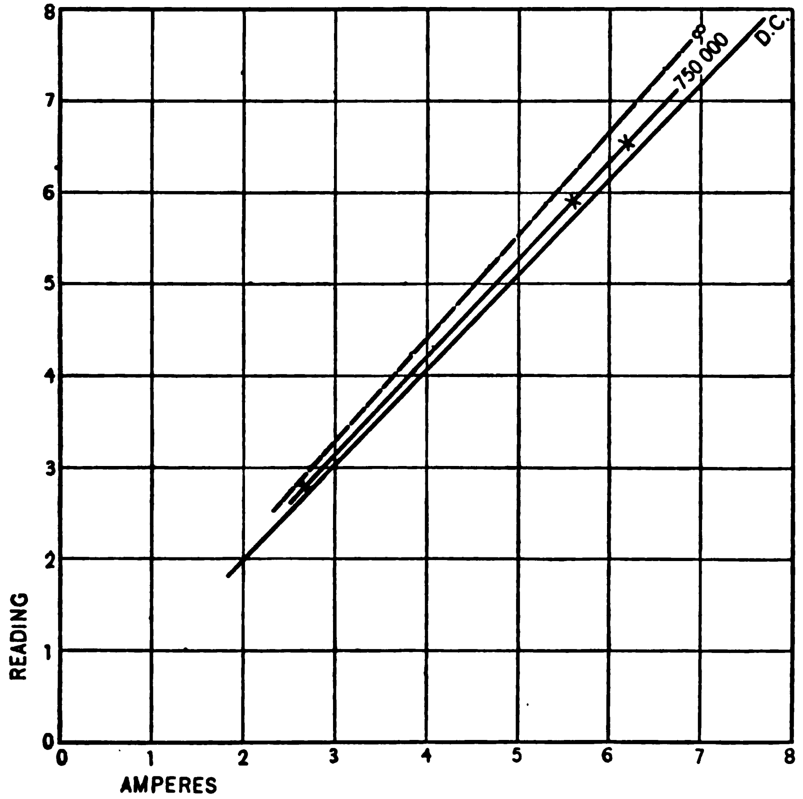

Fig. 25.—*Effect of frequency, six-section ammeter*

so that the resistance was not very much greater than the resistance of the copper wires in the two-section experimental instrument described above. The observed change of 3 per cent at 750 000 is therefore of the proper theoretical order of magnitude.

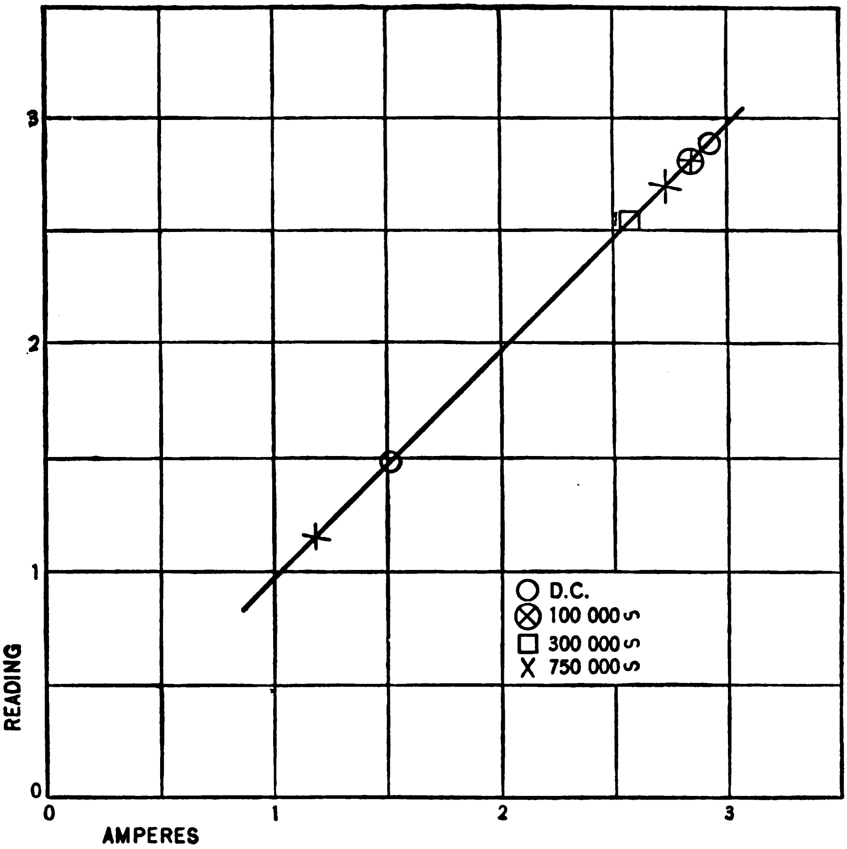

Fig. 26.—*Performance of instrument with two symmetrical sections*

The instrument was provided with a device for reducing its range, by opening the circuits at points *x*, *y*, *u*, *z*, putting the two halves of the hot wire in parallel. The range was then 3 amperes, while with six sections in parallel it should have been 9 amperes, with direct current or low-frequency current. The latter range, however, actually was 8.7 amperes, being reduced by the resistances in the connecting bars and wires (thus giving a hint of what was to be expected at high frequencies, when the inductances are all-important). Theoretical consideration of the instrument on low range, with merely the two halves of the hot wire in parallel, shows that there should be no changes of reading with frequency; and this was verified by observations at various frequencies, as shown in Fig. 26.

The results of measurements upon a commercial "unshunted" ammeter of two sections are given in Fig. 27. The diagram of this instrument is about the same as Fig. 19. Its indicating device was of the ordinary expansion type. At a frequency of 750 000 the reading was 7 per cent high, which is the order of magnitude that theory would lead us to expect.

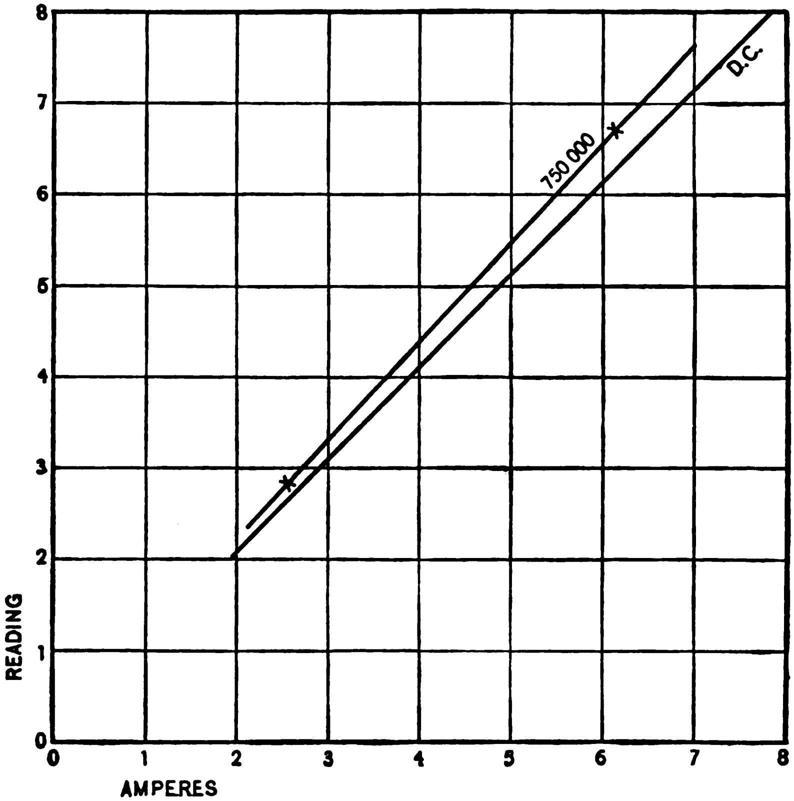

Fig. 27.—*Effect of frequency, commercial two-section ammeter*

5. SUMMARY

To sum up the investigation of the so-called unshunted type of hot-wire ammeter, it has been seen that this type is subject to serious errors, due to the self and mutual inductances of parts which have ordinarily been thought negligible, and that the errors can be predicted from a theoretical consideration of the impedances of the parts. These errors can be avoided in some cases by symmetrical location of the current leads. The errors can be eliminated in the range of radiotelegraphic frequencies by using hot wires of very high resistance, but not by using wires of moderate resistivity, such as platinum or bronze, especially if not kept to very small diameters. Since most of each current path is made up of bars or strips of very low resistance but very considerable inductance, the current distribution at a given frequency is more affected by the inductances than in the parallel wire type, and therefore the distribution for theoretically infinite frequency is practically reached at a much lower frequency.

Having found these various errors in the two types of ammeter employing hot wires, let us turn to a consideration of instruments in which the wires are replaced by a thin strip of metal.

V. THE STRIP AMMETER

By the use of a thin strip or sheet of metal instead of wires as the working resistance, an ammeter can readily be made to carry very large currents. Such instruments are coming into use in the high-power radio stations. The first requirement is that the strip be so thin that its resistance does not change with frequency. In the instruments whose deflections are produced by the expansion of the sheet of metal it is found in practice that the mechanical inequalities of a thin metal sheet make it necessary to use only a narrow strip as the indicating portion. As the sheet must have considerable width in order to carry large currents, it must therefore be slit or otherwise subdivided. Consequently the deflections depend on the current in one part of the sheet and not on the whole current. As the frequency is increased, the deflection changes as the current distribution changes. The errors are much larger than they would be if the deflections depended on the resistance of the whole sheet.

The changes of current distribution and resistance with frequency have not been theoretically worked out for thin strips of finite width, but from the experiments made some conclusions can be drawn.

1. EXPERIMENTS ON CURRENT DISTRIBUTION IN STRIPS

The first requirement of these instruments, viz, that the strip must be thin enough not to change in resistance with frequency was emphasized by the following experiments. A strip of phosphor-bronze 0.07 mm thick, 6.2 mm wide, and 11.1 cm long was soldered at the ends to two wires at right angles to the strips. Two rectangular portions at the middle were cut away, as shown, leaving three parallel strips 1 cm long and 1.2 mm wide separated by spaces of the same width. A thermocouple was soldered in turn on each of these three strips and the apparent change of current in each was observed for different frequencies. The results are summarized in Table 7.

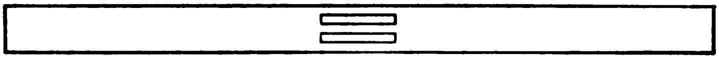

Fig. 28.—*Metal strip for investigation of current distribution*

TABLE 7

Per Cent Increase of Apparent Current in Phosphor-Bronze Strip

Frequency	150 000	500 000	1 000 000	1 500 000
	Per cent	Per cent	Per cent	Per cent
Middle strip............	+0.9	+4.6	+ 8.2	(+12.0)
Mean outside strip.....	+2.5	+8.6	+12.4	(+21.0)

The observations at 1 500 000 were made with insufficient sensibility and are uncertain, but all the results show a very marked increase of apparent current with increase of frequency, no matter at what point of the strip observations are made. This means a large increase of resistance with frequency. This effect would be much larger in a copper strip, and copper would have been used in this experiment, the purpose being to show the resistance change at its worst, but this could not be done because a copper strip with its low resistance did not get hot enough with the currents used to give measurable deflections. The resistivity of the phosphor-bronze was four times that of copper.

The foregoing experiment illustrates another effect, viz, the tendency of the current at high frequencies to crowd toward the outer edges of the conductor. In fact, the difference between the current in the middle and the outer strips was really greater than appears from Table 7, because the convection and conduction of heat tended to equalize the temperatures.

It would be expected that in strips of higher resistivity the changes of resistance and of current distribution would be less. This was proved by repeating the above experiment with a strip of high-resistance metal—resistivity thirty-six times that of copper. The dimensions were the same as in Fig. 28, except the thickness, which was 0.03 mm. The results of measurement were:

TABLE 8

Per Cent Increase of Current in High-Resistance Strip

Frequency	500 000	1 000 000	1 500 000
	Per cent	Per cent	Per cent
Middle strip		−0.5	−1.7
Mean outside strip	0.0	+0.3	+0.9

It appears that the strip is thin enough and the resistivity great enough so that there is no appreciable change of resistance up to 1 500 000. The change of current distribution, however, is perceptible, and is really greater than the results show, because of heat conduction and convection. Since the deflection of an ammeter depends on the temperature of the indicating strip, this equalization of temperature over the strip is actually an advantage, reducing the effects of change of current distribution. In the ammeters described below, the parts of the strip were not separated by spaces as wide as 1 mm, as in the present experiment, so the temperature differences would be still less. Finally, since ammeters for such large currents would rarely be used for frequencies as high as 1 000 000, it may be said that in an ammeter with the working strip made of this high-resistance metal no error is introduced by the strip itself.

2. EFFECT OF TERMINAL BLOCKS

Measurements were made on a simple ammeter of the strip type. A side view of the instrument is given in Fig. 29. B and B′ are massive brass blocks of square cross section. S is a vertical thin strip of resistance metal, soldered at the ends into the brass blocks. The strip is 0.07 mm thick, and the resistivity is about the same as that of the strip studied in the preceding paragraph. The mechanism for indicating the expansion is attached by a wire to the point I. The strip is slit as shown, so that only the expansion of the center portion is measured. The large brass blocks help to dissipate the heat, which is the main concern in an ammeter for large currents. The results of measurements are given in Fig. 30. As shown, its readings decreased 11 per cent at 750 000 and 4 per cent at 300 000, and were practically the same at 100 000 as on direct current. This result is surprising, in view of the conclusion reached above, that the changes of current distribution in strips of this high resistivity should be negligible. All is explained when the massive terminal blocks are considered. The resistance of these is insignificant compared to the resistance of the strip, but their inductance is certainly comparable with that of the strip. For one thing, the path of the current in the blocks is longer than in the strip, and, moreover, is not of exceedingly greater cross section, because at these frequencies it is known that the current flows in a thin skin on the surface of such conductors. Thus more current will be flowing to the outer edges of the thin strip than to its middle portions.

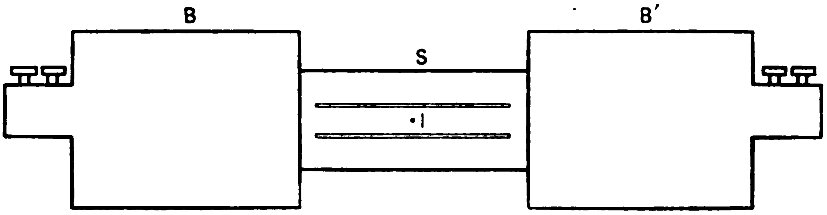

Fig. 29.—*Strip ammeter with rectangular terminal blocks*

While the readings decreased when the expansion of the middle portion was measured, they should increase if the expansion of the upper or lower part of the strip were measured. It seemed worth while to verify this experimentally, and to do so the indicating mechanism was attached to a point on the upper part of the strip instead of at the point I. The readings then *increased* 8 per cent at 750 000 and 4 per cent at 300 000. The changes of current distribution are really larger than the results indicate, because the temperatures of different parts of the strip are equalized to a considerable extent by heat conduction and convection. The existence of the heat flow between parts at different temperatures is verified by the fact that on high frequency the reading was observed to come up to its final value more slowly than on low frequency for which the heat production was the same in all parts. Furthermore, the effect of convection could be reduced by placing the strip in a horizontal plane, when the observed change from low to high frequency should increase. This was

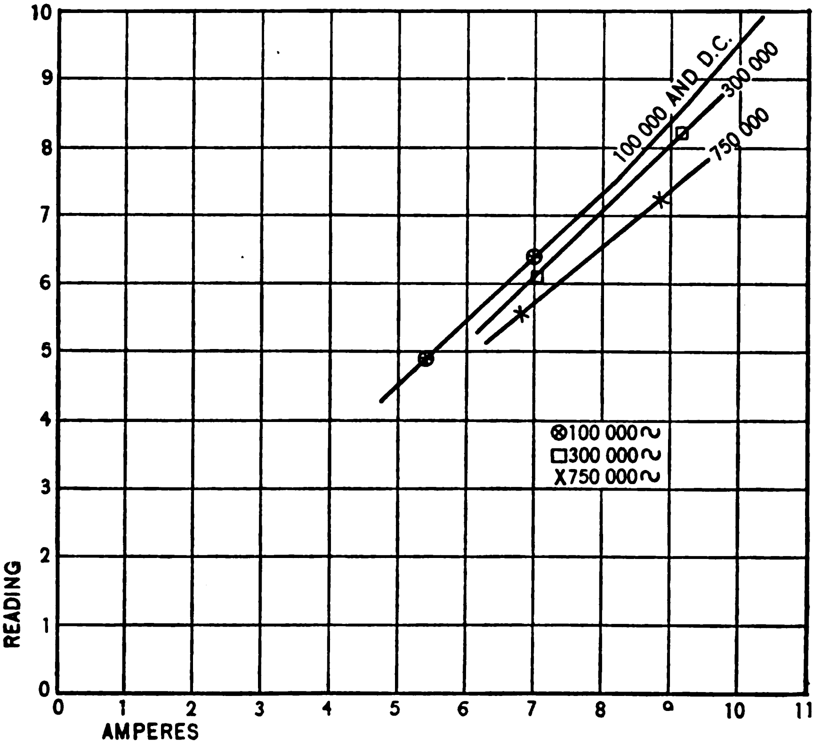

Fig. 30.—*Effect of frequency, strip ammeter*

tried, and the increase was found to be 1 per cent, both at 750 000 and 300 000.

The terminal blocks can be so designed as to reduce their effect on the current distribution across the thin strip . For example, an improvement in this direction is to make the blocks wedge-shaped as in Fig. 31. The top sketch is a top view and the following one a side view of another ammeter tested. As the current passes along the block toward the strip, it tends more and more to become distributed uniformly with respect to the breadth of the strip. The results of measurements are plotted in Figs. 32 and 33 for two instruments of this type having strips 0.03 mm thick and of the same resistivity as before. There is no change of reading at 100 000 and 300 000, and at 750 000 the decrease is somewhat less than 3 per cent. The shaping of the terminal blocks decidedly improves the instrument.

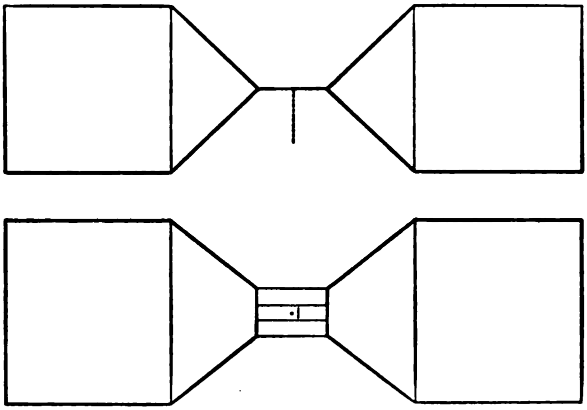

Fig. 31.—*Strip ammeter with wedge-shaped terminal blocks*

A still further improvement is found in the instrument represented in diagram in Fig. 34. This design is due to Mr. F. W. Roller. The thin strip is soldered at its ends to rather long rods, at opposite ends of which the current is introduced. Each part of the strip has in series with it about the same amount of rod impedance, and hence no change of current distribution should take place. This was confirmed for frequencies up to 750 000.

The changes of current distribution with frequency in the terminal blocks of strip instruments are the counterparts of the

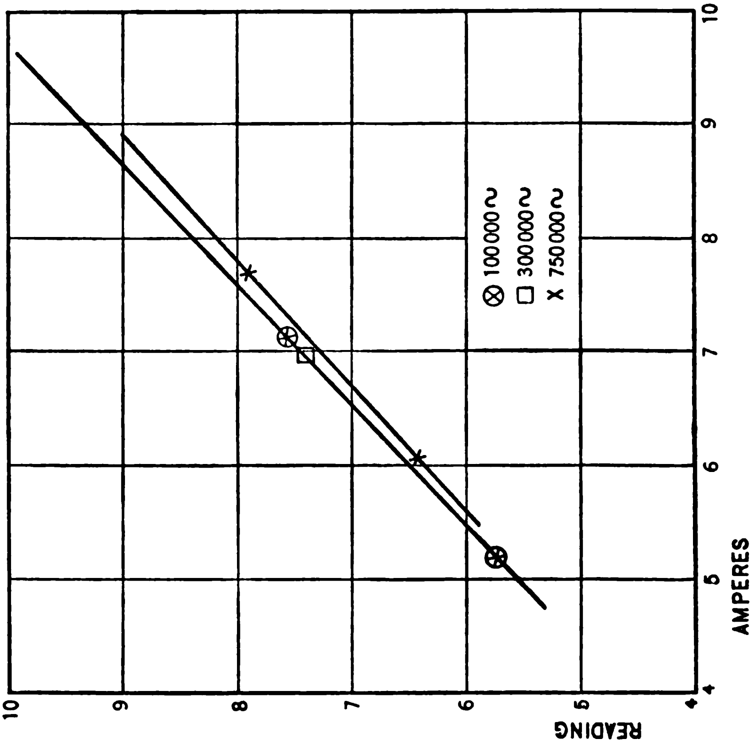

Fig. 32.—*Effect of frequency, wedge-block ammeter*

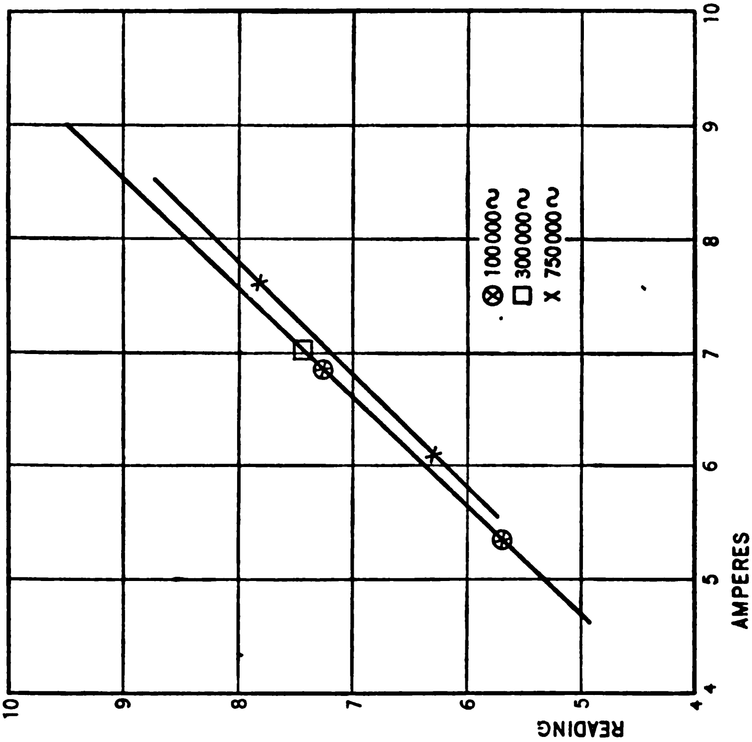

Fig. 33.—*Effect of frequency, another wedge-block ammeter*

effects in wire instruments due to the self-inductances of parts other than the hot wire, e. g., Figs. 14 and 19. The remedy, the type of current lead shown in Fig. 34, is the counterpart of the disposition of leads suggested in Fig. 15.

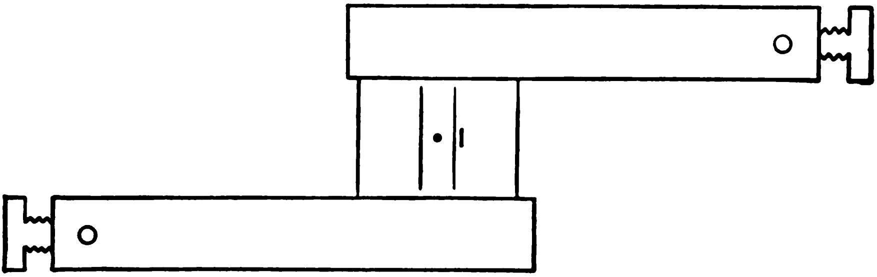

Fig. 34.—*Strip ammeter with rod terminals*

3. CYLINDRICAL ARRANGEMENT

An instrument which avoids most of the difficulties is one in which strips are arranged in parallel equidistantly on a cylindrical surface, so that each has the same set of mutual inductances with respect to the others. This is the same principle as in the wire instrument shown in Fig. 16. If the strips are put closer and closer together this type approaches the limiting case of a thin tube, which theoretically has uniform current distribution on high and low frequencies. Such an instrument employing strips, the expansion of one of which is measured, has been designed by R. Hartmann-Kempf [16] and is now on the market. The strip must be thin enough and of such high resistivity that it does not change appreciably in resistance at the frequencies used. It is very difficult in practice to get such thin strips of uniform thickness, so that the resistances of the strips are likely to differ, although the inductances would be equal, which would cause considerable changes of reading with frequency. Strips of platinum or of platinum-rhodium are used in such instruments because of their excellent thermal qualities, but their rather low resistivity makes them subject to this source of error. This kind of strip instrument was not tried out because none was available to the writer, but its principle and performance are illustrated by the instrument of Fig. 16.

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[16] See footnote 7, p. 107.

4. SUMMARY

To summarize the consideration of the strip ammeter, the thin strip with its terminal blocks or other leads is a complex problem. By using thin enough strip of high enough resistivity the effects of resistance change and current distribution within the strip itself can be made negligible, but the current distribution in the terminals may greatly alter the current distribution in the strip at high frequencies. This can be avoided by suitable shaping and connection of the terminals. A good way to avoid the errors is to arrange strips in parallel on the surface of a cylinder. Great care is necessary to see that the different strips in this arrangement are sufficiently uniform in resistance.

In concluding the description of this investigation the author desires to express his thanks to Prof. E. B. Rosa, of the Bureau of Standards, and to Prof. E. P. Adams, of Princeton University, for their helpful encouragement, and to Mr. F. W. Roller, of New York City, for the loan of instruments.

VI. CONCLUSIONS

1. The circuit within a high-frequency ammeter must be of as simple form as possible. This requirement is best fulfilled by a single straight wire of very small diameter, and no other arrangement can be taken as à priori reliable at all frequencies. The heat production is readily measured in any form of circuit, and in consequence all successful ammeters for high frequency utilize the thermal effect. The thermometric means of measuring the heat production, whether expansion, calorimetric effect, resistance, or thermal emf, does not affect the accuracy. Two similar wires in parallel, the integrated heat production in the whole being measured, constitute a system nearly as reliable as a single wire. With such a system, in an oil bath, currents up to 10 amperes can be measured. For larger currents other combinations of current elements are necessary, and a great variety of ammeters have been developed and have been studied experimentally and theoretically in this investigation. Experimental instruments, and commercial instruments of three different companies, have been included. All the types in use are subject to errors when

used at the frequencies of radiotelegraphy, the errors being in some cases very large. In some the readings increase with increase of frequency and in others decrease. In most cases the design can be so changed as to eliminate the errors.

2. The current *in a conducting circuit* has no meaning for extremely high frequencies; for in any circuit, above a certain high frequency, the capacity between parts of the circuit and of auxiliary apparatus is so important that an appreciable fraction of the current is shunted through the dielectric and the current is of different amount in different parts of the wire circuit. This was demonstrated for the circuits used in these experiments at a frequency of 1 500 000 (wave length = 200 meters); for the current was found to be different in two ammeters in series, because of the large capacities to earth of lead wires and galvanometers. The apparent errors due to this effect were of the order of 5 per cent. A way was found to eliminate the effect, for the purposes of ammeter comparison.

3. The changes of current distribution, in the instruments whose working parts were of low-resistivity metal, all occurred in about the range of radiotelegraphic frequencies, 100 000 to 1 500 000. That is, the current distribution was constant for frequencies from 0 up to about 100 000, then underwent changes and became constant at different values for frequencies above about 1 500 000. The agreement of the range of these changes with the frequencies of radiotelegraphy is a remarkable coincidence. For these instruments and the circuits used, in view of this fact and conclusion (2), just above, it may be said that 1 500 000 is physically infinite frequency in two senses.

4. The order of agreement found between theoretical calculation and experiment shows that the ordinary formulas for self and mutual inductances of finite linear parts of a circuit hold for the short lengths used. In view of the frequencies used and the fact that the oscillations were somewhat damped, this is one of the more interesting results of the work from the standpoint of pure science.

5. An approximate experimental method for investigation of the current distribution in thin strips at high frequency has been devised, and used to obtain qualitative results. Further

investigation of thin strips as to current distribution and resistance, both experimentally and theoretically, is recommended as a subject for research. The subject will increase in importance, for probably more current can be carried with a given skin effect error by a thin strip than by a round wire of the same cross section.

6. Most of the errors of commonly used high-frequency ammeters have been found to be due to the mutual inductances, or to self-inductances of parts, which had been supposed negligible

7. Some errors which have been suspected were found negligible. Eddy currents in adjacent masses of metal were found to produce no effect. The inductive actions of distant parts of the circuit and of the leads when brought straight in to the instrument were found negligible. In some cases the leads do change the readings appreciably, when close to and parallel to the working parts of the instrument, and some caution in regard to them is therefore necessary.

8. The use of high-resistance metals in the working parts, *keeping them of very small cross section*, eliminates errors in most cases. This expedient has the effect of moving the changes of current distribution up to frequencies higher than those with which it is desired to work. However, other considerations sometimes make the use of larger cross sections or of the lower resistivity materials desirable. In these cases, then, the effects of current distribution may be appreciable at ordinary working frequencies.

9. The location of the current leads is of great importance, particularly in the so-called unshunted ammeter, determining whether the error shall be large or inappreciable.

10. All errors due to inductive action of the leads can be avoided by bringing them in at right angles to the plane of the instrument. This is a very helpful arrangement in experimental instruments made to isolate and study particular effects.

11. In the hot-strip ammeters, if the strip be thin enough and of sufficiently high resistivity, the observed errors depend entirely on the current distribution in the terminal blocks, and can be eliminated by proper design.

12. An instrument free from theoretical objections consists of current elements arranged equidistantly on a cylindrical surface, the leads being brought in to the middle points of the ends of the cylinder. The current elements may be fine wires, or they may be replaced by thin strips of considerable width or by a continuous thin tube. The instrument has the limitation treated in the next paragraph, in common with the other types of ammeter.

13. The most insidious error of all is nonuniformity of resistance of the working parts, in any ammeter for large high-frequency currents. Two wires or strips of the same length and approximately the same cross section will have the same self-inductance, but the resistances may be quite different because of variations of hardness and small variations of cross section. Thus they may carry exactly the same currents at high frequency, but very different currents at low frequency. This error arises from the difficulty of obtaining and preserving wires and strips of such small cross section sufficiently uniform. This error was rather unexpected, but was surprisingly evident in a number of cases investigated. The practical result is that any high-frequency ammeter whatever, employing more than a single fine wire, is subject to change of current distribution.

14. These experiments furnish very good illustrations of the fact that the changes of current distribution within a particular system are changes of the first order of magnitude, compared to which the change of resistance of the whole is of the second order. By taking advantage of this principle, it has been shown that some of the types of ammeters can be greatly improved.

15. In conclusion, the various effects which determine the deflections of high-frequency ammeters have been isolated and critically studied, by experiment and by the aid of theoretical calculation. Some sources of error which had been suspected were found negligible, and some other effects were found to produce errors of surprisingly great magnitude. Ways of eliminating the various errors have been given.

WASHINGTON, April 3, 1913.

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FEBRUARY 20, 1914

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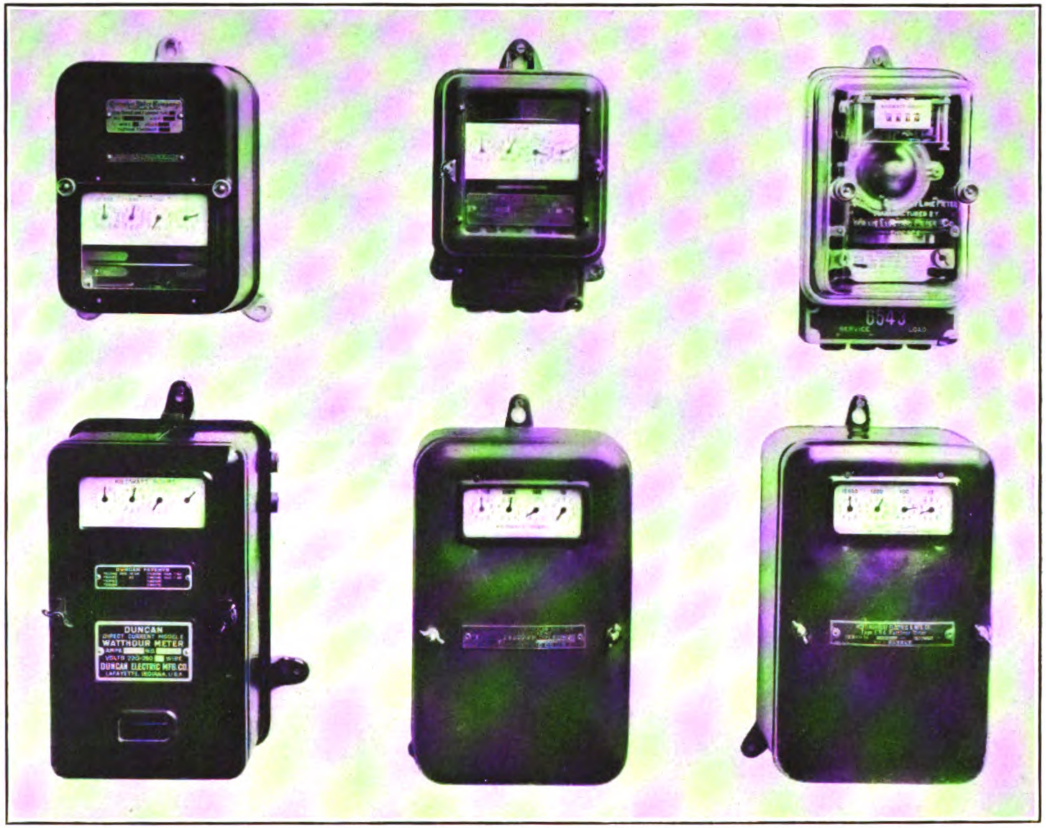
DUNCAN
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WATTHOUR METER
DUNCAN ELECTRIC MFG. CO.
LAFAYETTE, INDIANA, U.S.A.
6543
SERVICE
LOAD

Fig. 7.—*Meters complete*

A COMPARATIVE STUDY OF AMERICAN DIRECT CURRENT WATTHOUR METERS

By T. T. Fitch and C. J. Huber

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I. INTRODUCTION

Although many excellent discussions of the watthour meter have been published, it was thought that a thorough study of all American makes of a given type of meter, made at the same time, would be of considerable interest and value. In order to obtain such data each of the six American manufacturers of direct-current watthour meters was requested by the Bureau of Standards to submit three 5-ampere, 220-volt, 3-wire meters for a comparative test.[1] In most cases the results given in the following discussion are the average values obtained from tests of three meters.

It should be stated at the outset that this test was not intended to be competitive. No attempt has been made to rank the meters according to the results of the tests.[2] Any such grading is very likely to be misleading as the various features studied are of unequal importance. Moreover, the characteristics required for different kinds of service are unlike and would be weighted differently by different engineers. It must be noted that while laboratory tests are valuable, they do not form a sufficient basis upon which to pass final judgment on a type of meter. For such a purpose practical experience with meters is necessary, such as is best obtained in central-station practice.

II. PERFORMANCE DATA

1. **Load Curves.**—Before any tests were made the meters were inspected to see that they were in proper running order. They were then adjusted to be as nearly correct as practicable at the 10 per cent and 100 per cent loads.

In this discussion the load curve of the watthour meter is the plot of the rate against load, the rate being defined as the ratio of the watthours recorded by the meter to the actual watthours. Such a curve has generally been considered perfectly definite if the tests are made at standard temperature and voltage is kept on the potential coil long enough for it to reach a steady state. It was found, however, in this test that the heating effect of the series coils is by no means negligible. Evidently then the load curve obtained for a watthour meter depends to an appreciable extent on the time which is allowed to elapse after putting each load on the meter. In this discussion the electrodynamic load curve will be defined as one taken in so short a time that the heating effect of the series coils is negligible. In practice this can be very nearly realized by taking quick comparisons of the rate at a given load with the rate at some one load as a standard; or, in other words, by alternating the readings at the two loads. In an actual test of this kind usually five checks of the meter rate are taken, alternately at the standard load and the load to be compared. This makes three checks at the standard load and two at the other load. This procedure is then repeated for another load and the standard load, and so on. The full lines in Fig. 1 are curves obtained in this way, corrected to make the 10 per cent and 100 per cent load points correct. Where corrections of this sort were made it was done on the assumption that shifting the magnets moves the load curve parallel to itself, while adjusting the starting device changes the rate by an amount inversely proportional to the load. Some tests made on this point, of which the results are shown in Table 1 and discussed in paragraph 10 bear out the assumption closely except for meter D, and for this meter such correction was not attempted. The dotted lines in the same figure show the effect of the heating of the series coils in distorting the load curve. Here again the 10 and 100 per cent load points were adjusted to be correct. In Fig. 2 are given what may be termed the "ordinary" load curves; that is, no particular attention was paid to heating of the series coils, the points being taken

---

[1] Exception was made for the Sangamo meter, as the smallest direct-current meter manufactured by the Sangamo Electric Co. is of 10 amperes capacity.

[2] Letters are used as a matter of convenience to designate the different manufacturers as follows: A, Columbia Meter Co.; B, Duncan Electric Manufacturing Co.; C, General Electric Co.; D, Sangamo Electric Co.; E, Westinghouse Electric & Manufacturing Co.; F, Willis Electric Meter Co. All of these meters are of the commutator motor type excepting D, which is a mercury meter.

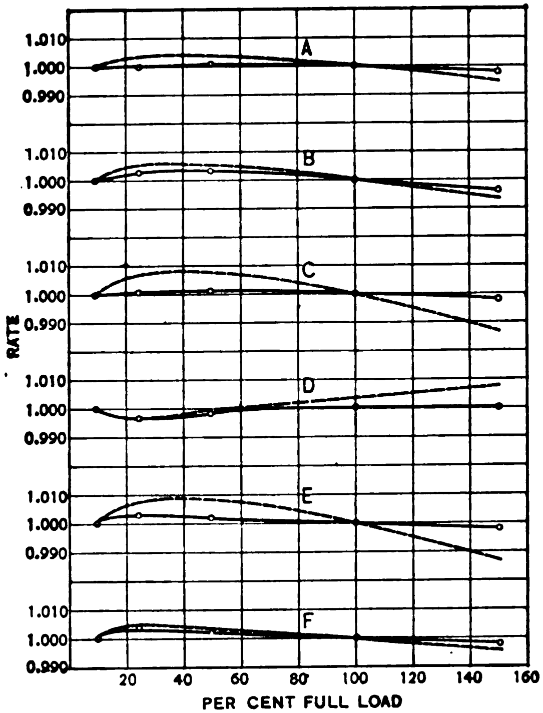


Fig. 1.——— *Electrodynamic load curves.* ------ *The same with added effect of series coil heating*

in as rapid succession as could be conveniently done, beginning at the light load. As before, corrections were applied to make the 10 per cent and 100 per cent load points correct, except for meter D. In section 16 will be found a further discussion of the load curves.

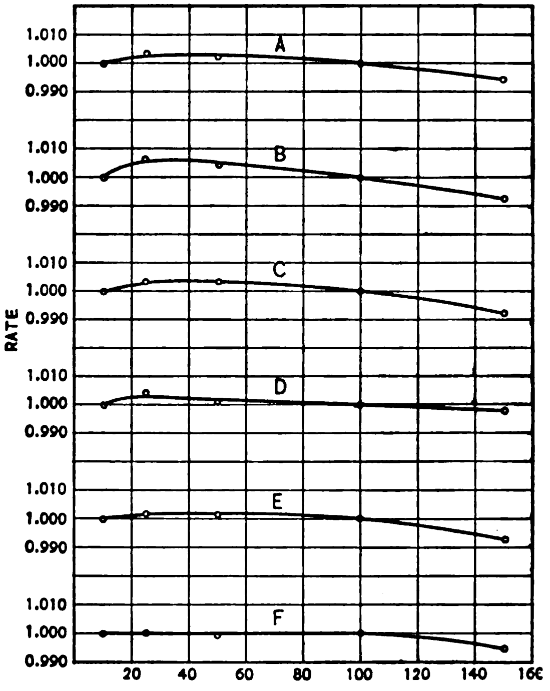


Fig. 2.—*Ordinary load curves*

To determine the magnitude of the heating effect of the series element, a given load was held by means of a potentiometer after the potential circuit had come to a steady temperature and an automatic record of the revolutions of the meter was taken on a chronograph. From this record the rate of the meter at the beginning of the run could be obtained and the change in rate followed until no further change was noticeable. Such records were taken at several loads to determine the relation between the total change in rate and the load current. This change was found to be very nearly proportional to the square of the current. Fig. 3 is a typical chronograph sheet showing the change in rate of a meter with the lapse of time after closing suddenly on 150 per cent of full-load current. The chronograph drum made one revolution in 60 seconds; the vertical lines mark 5-second intervals. The curve is drawn through points indicated by a given number of revolutions of the meter disk. This curve would continue in the straight line AB if the rate of the meter had remained constant, but due to the heating of the series coil the rate decreased until the curve

TABLE 1

Performance of Watthour Meters

Watthour meter	A	B	C	D	E	F
Rated full load R. P. M.	33.0	36.7	45.8	27.5	45.8	55.0
Per cent difference in balance of current elements:						
No. 1	1.1	5.1	0.4	....	0.6	2.6
No. 2	3.2	1.5	1.6	....	0.0	3.2
No. 3	4.2	3.6	0.8	....	0.8	0.3
Per cent change from reversing stray field of 1 gauss at full load	2.2	2.2	2.3	0.0	2.6	2.7
Per cent change from removing covers:						
Heating [3]	+0.3	+0.1	+0.6	0.0	+0.7	0.0
Magnetic	+0.2	0.0	−0.4	0.0	−0.3	0.0
Per cent change from reversing polarity:						
50 per cent load	0.8	0.6	0.5	2.9	0.9	0.5
100 per cent load	0.5	0.3	0.2	1.9	0.4	0.2
Polarity marked	Yes	Yes	No	No	Yes	Yes
Range of light-load adjustment, per cent	4.6	5.6	13.8	4.6	22.0	12.2
Range of full-load adjustment, per cent	86	155	68	35	92	65
Per cent change of full-load rate by maximum change of light-load adjustment	0.5	0.3	0.7	−1.5	1.5	1.1
Per cent change of light-load rate by maximum change of full-load adjustment	85	154	66	38	104	65
Per cent change from short circuit on 120 volts	2.5	2.9	1.1	2.3	1.9	−2.2
Maximum amperes on 120-volt short circuit	240	260	260	>500	270	340
Per cent change by short circuit on 240 volts	34.0	11.6	5.6	0.0	4.7	−3.4
Maximum amperes on 240-volt short circuit	400	400	430	730	440	560
Full-load back emf, in volts	0.13	0.13	0.19	0.0001	0.17	0.07
Starting current, in amperes:						
No. 1	0.06	0.02	0.04	....	0.09	0.08
No. 2	0.07	0.06	0.05	0.02	0.07	0.04
No. 3	0.07	([4])	0.03	....	0.08	0.11
Creeping voltage, in volts:						
No. 1	130	120	130	160	130	130
No. 2	130	130	130	260	130	130
No. 3	130	100	130	180	130	130

[3] The plus sign indicates an increase in speed.

[4] Where no figure is given of the starting current it indicates creeping on voltage only.

coincided with the line CD. The dotted curves in Fig. 1, already referred to, were obtained from runs of this kind. The method of getting an automatic record of the rate of the meter on a chronograph sheet is described on page 174.

2. **Voltage Curves.**—In testing the meters for variation of rate with voltage they were run at full-load current and different voltages, each voltage being held a sufficient time for the resistance of the potential circuit to attain a constant value. The curves plotted in Fig. 4 show the results of the test. The rate of the meters is less at higher voltages; this effect is primarily due to the heating of the potential circuits, which have necessarily a large temperature coefficient. It should be noted that this performance would be slightly different at other loads, owing to the relatively larger effect of starting coil compensation at lighter loads.

TABLE 2

Temperature Coefficients (Per Cent per Degree C)

Watthour meter	A	B	C	D	E	F
Potential circuit	+0.17	+0.35	+0.41	+0.30	+0.41	+0.38
Disk	+ .39	+ .38	+ .39	+ .40	+ .37	+ .38
Magnets	− .03	− .01	− .01	− .01	− .02	− .03
Algebraic sum [a]	+ .28	+ .05	.00	+ .12	.00	+ .06
Meter	+ .26	+ .10	+ .10	+ .12	+ .07	+ .11

[a] In taking the sums, the coefficients of magnets were doubled and the sign reversed for both potential circuit and magnet coefficients.

3. **Temperature Coefficient.**—The temperature coefficient of a watt-hour meter depends upon the temperature coefficients of the potential circuit, the disk, and the drag magnets. Nearly complete compensation for temperature variations is ordinarily attained by making the temperature coefficients of the disk and potential circuit equal, as they affect the meter in opposite directions. This leaves outstanding the temperature coefficient of the magnets; this, however, is usually small. Table 2 gives the over-all coefficients of the meters and also the coefficients of the parts. It may be pointed out that the temperature coefficient of the meter depends directly on the algebraic sum of the coefficients of the disk and potential circuit but on twice the coefficient of the magnets. This is true because the rate of the meter is inversely proportional

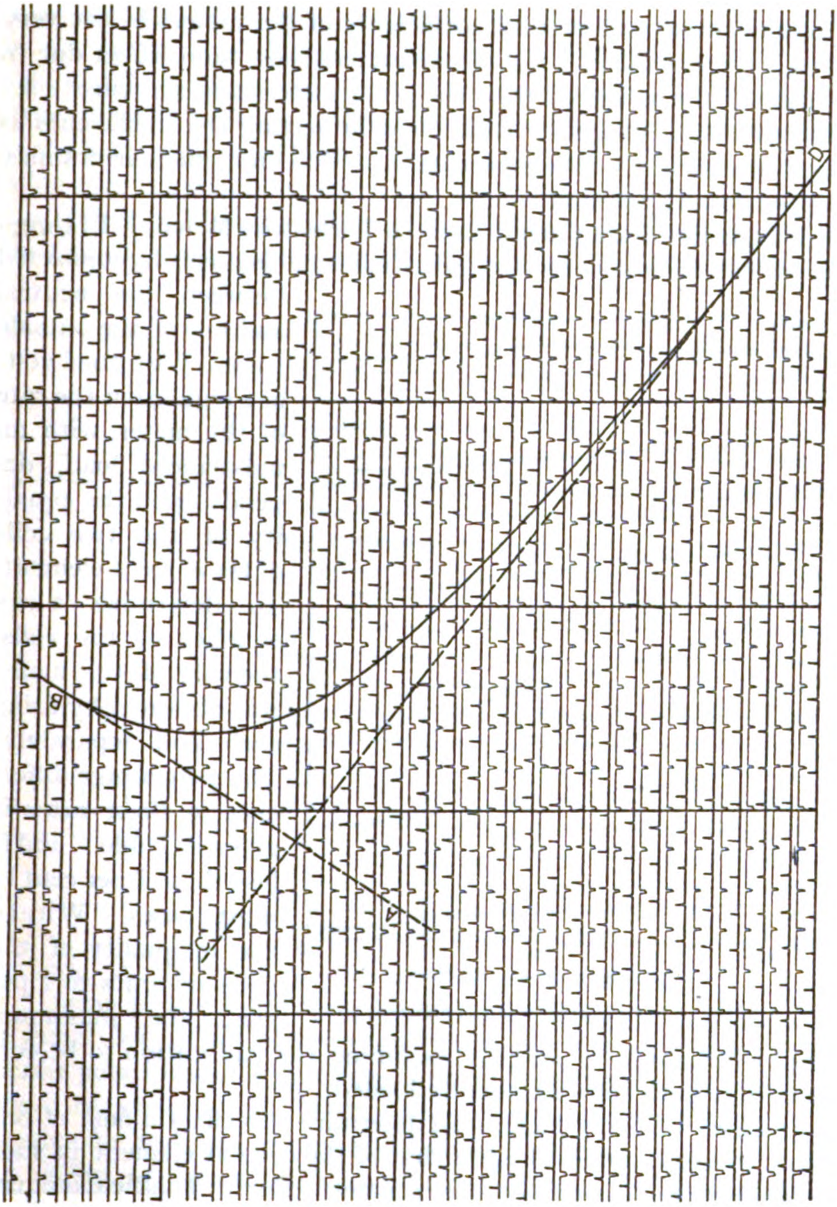


Fig. 3.—*Typical chronograph record showing heating effect of series coils*

to the square of the flux in the magnets. The check between algebraic sums and over-all coefficients of the meters is not very close for meters C and E. These meters show more effect due to heating of the series coil than the other meters and this effect may not have been altogether eliminated in getting the coefficients as watthour meters. In a summation of this kind small errors may happen to add together.

4. **Equality of the Current Coils in Three-wire Meters.**—In three-wire direct-current meters the potential circuit is generally connected between the neutral and one of the outside wires. With good voltage regulation the rate of the meter, with an unbalanced load, depends upon the equality of the two coils of the current element. To determine this equality of the coils, the rate of the meter was obtained by using each coil separately. The percentage difference in these rates is given in Table 1, and is less than 2 per cent in most cases. Where the inequality of the coils amounts to 2 per cent the maximum error will be only 1 per cent, assuming the calibration to be correct when both coils are equally loaded.

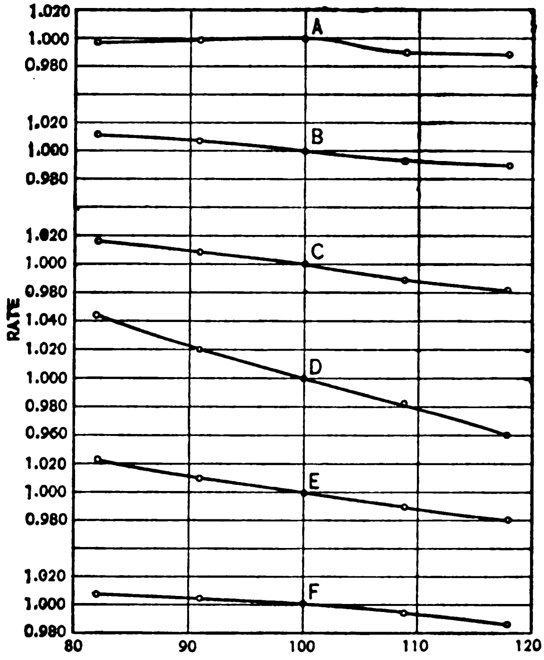
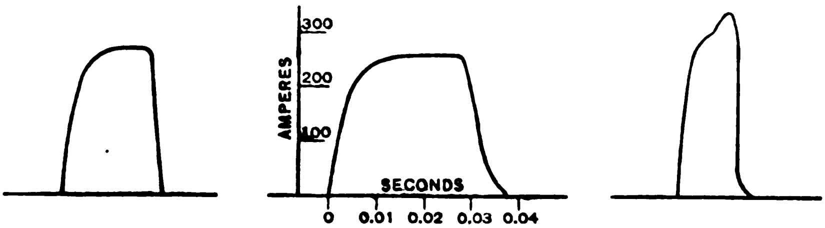


Fig. 4.—*Variation of rate with voltage*

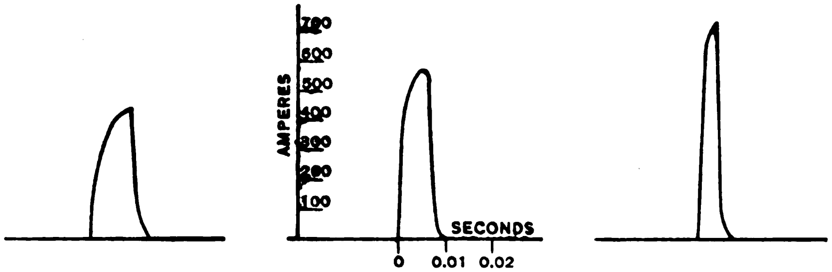
5. **Effect of Stray Field.**—To determine this effect a field of one gauss was superimposed upon that of the current element in such a manner as to produce the greatest effect. This field is equal to that at a distance of 25 centimeters from a straight conductor carrying 125 amperes, and is about five times the horizontal component of the earth's field at Washington.

In Table 1 is given the percentage difference in rates due to reversing this field. This percentage change in rate should be equal to the percentage change in the meter field due to the stray field. This is seen to be very nearly true from the values of field strength given in Table 3, which are necessarily only approximate, as the fields are not uniform. The values given are for the average fields over the spaces in which the armatures rotate.

6. **Effect of Reversing Polarity.**—As meters are usually tested in position it is an open question whether the polarity should be marked. All the meters have the polarity marked except C and D. Owing to the thermocouple method of light-load adjustment on meter D it is clearly necessary to connect it in circuit with definite polarity, and it therefore appears desirable that its polarity should be marked. In Table 1 are given the effects of reversing polarity for both 50 per cent and full-load current.



SHORT CIRCUIT ON 120 VOLTS



SHORT CIRCUIT ON 240 VOLTS

Fig. 5.—*Oscillograms of short-circuit currents*

7. **Effect of Covers.**—When a meter is tested in position it is usually necessary to remove the cover and often necessary to test it with the cover off. It is then a matter of importance to know what change in rate is caused by the removal of the cover. The

change in the rate may be due either to magnetic material in the cover or to temperature changes.

In Table 1 will be found the results of this test. Meters C and E, which show the largest amount of the magnetic effect, each have a small piece of sheet iron to hold the glass window in front of the dials.

8. **Effect of Short Circuits.**—As meters in service are always liable to be subjected to accidental short circuits, they should be constructed so that they will be as little affected as possible. To determine the magnitude of this effect the rate was obtained after ten times the full-load current had been passed through the meter. None of the meters was appreciably affected. The rate was also obtained after the meter was short-circuited through a fuse on 120 and then on 240 volts. The percentage change in rate is given in Table 1. Figure 5 shows some typical oscillograms which were taken in each case to determine the maximum current.

9. **Starting Current and Creeping Voltage.**—The current required to start the meters at normal voltage and the voltages required to make the meters creep when no current passes through the current element are given in Table 1. In most of the meters it is seen that the starting current is of the order of 1 per cent of the full-load current. Very small starting current is not necessarily a good feature, as it may indicate too small brush pressure for good contact. The values of brush pressure for one meter of each type are given in Table 4. As this pressure may vary widely even among meters of the same make, the values given are useful only in indicating the order of magnitude.

TABLE 3

Constants of the Coils

Watthour meter	A	B	C	D[a]	E	F
Resistance of potential circuit in ohms:						
Multiplier	3080	1340	....	....	....	....
Starting coil	230	12	1790	....	1710	....
Armature	2300	1290	930	....	980	1360
Total	5610	2640	2720	5290	2690	4580
Potential circuit watts	2.2	4.6	4.4	9.2	4.5	2.6
Current element: Resistance, ohms	.26	.23	.23	.002	.21	.10
Watts loss, full load	6.5	5.7	5.7	0.2	5.2	2.5
Flux density full load, gausses	70	85	75	....	70	85

[a] Rated voltage of meter D was 220; of the others, 110.

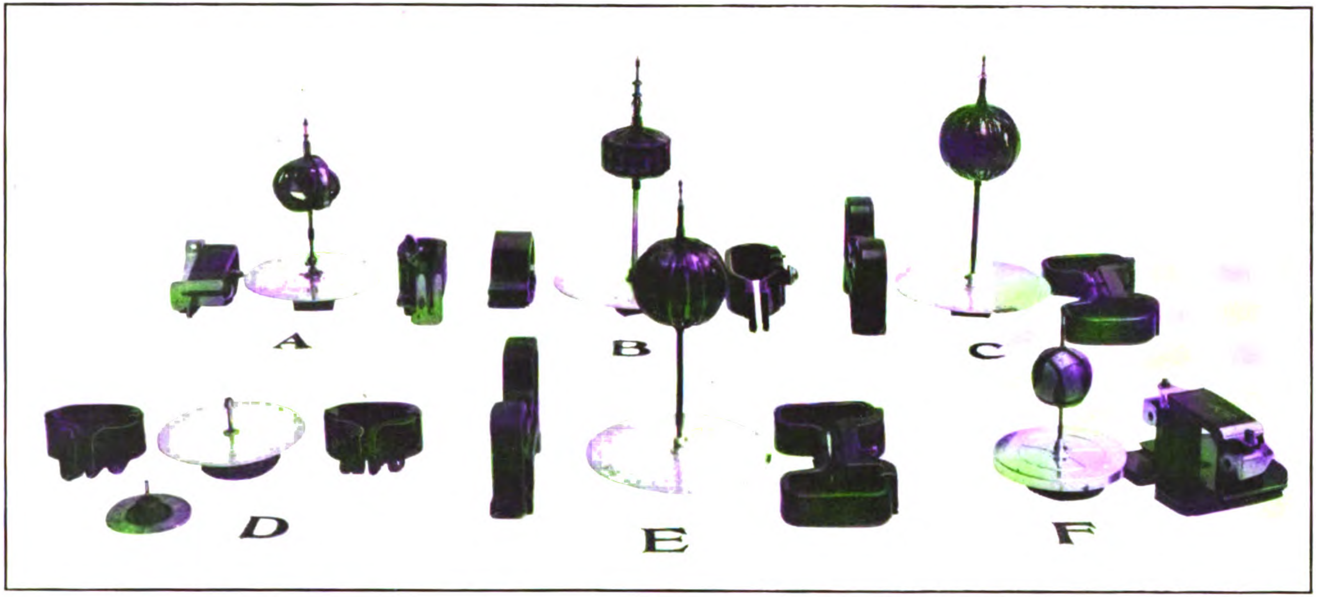


Fig. 6.—*Moving elements and magnets*

TABLE 4

Constants of Moving Elements

Watthour meter	A	B	C	D	E	F
Torque in cm-g	7.47	14.31	16.69	3.92	14.92	2.85
Weight in g	98.4	156.2	101.8	7.2	96.1	97.4
Ratio of torque to weight	.076	.092	.164	.545	.155	.029
Diameter of commutator, cm	.265	.465	.240	....	.240	.195
Number of commutator segments	3	8	8	....	8	3
Thickness of disk, cm	.115	.150	.065	.090	.065	.115
Diameter of disk, cm	11.40	13.35	12.66	10.18	12.70	8.54
Voltage drop across armature with 110 volts on potential circuit	45.1	53.8	37.6	....	40.1	32.7
Brush pressure, g	.24	.57	1.5	....	1.8	.34

TABLE 5

Constants of Magnets

[The dimensions are given in centimeters and the flux densities in gausses]

Watthour meter	A	B	C	D	E	F
Number of magnets	2	2	4	2	4	1
Steel:						
Length, l_m	19.4	26.2	23.2	18.1	24.0	13.3
Cross section, q_m	2.2	2.0	1.4	2.2	1.4	2.5
Air gap:						
Length, l_a	.28	.36	.24	.29	.25	Adjustable
Cross section, q_a	5.3	6.8	4.4	3.1	4.4	2.5
$K = l_m/q_m + l_a/q_a$	167	247	304	88	302	....
Total flux	9700	14400	7300	8100	7300	[7] 1300

[7] Taken with 2.5-mm air gap.

10. **Range of Adjustments and Their Mutual Effects.**—In Table 1 it is seen that the range of the full-load adjustment is large compared with that of the light load, also that full-load adjustment shifts the whole-load curve, while the light-load adjustment shifts each point by an amount very nearly inversely proportional to the load. In the case of meter D, an increase in the rate at light load due to the shift of light-load adjustment caused a decrease in the rate at full load. This peculiarity is due to the thermocouple method of light-load adjustment. This arrangement consists of a thermocouple, heated by the potential circuit coil, which sends an auxiliary current through the mercury chamber. In other words,

this circuit is a shunt circuit on the mercury chamber. At low values of the main current this circuit adds to the current through the mercury chamber, but when the IR drop of the main current reaches a value equal to the thermocouple emf the auxiliary current becomes zero and for still higher values of the main current some current is forced backward through the thermocouple, making a reduction in the driving torque.

A large range of light-load adjustment is convenient for the meter tester, but this has its disadvantages. Too great a range of light-load adjustment will permit the meter to be adjusted to be correct when there is excessive friction and the meter should be either repaired or removed.

III. DETAILS OF CONSTRUCTION

11. **The Moving Elements.**—The main constants of the moving elements are given in Table 4. Each value of torque given is the average of 10 values reduced to 25° C, obtained with the rotating part in 10 positions, one-tenth of a turn apart. These measurements were taken with full-load current and normal voltage of 110 or 220 volts. It may be mentioned that when a meter is rated for a range of voltages, the highest voltage is generally used in measuring the torque.

12. **The Magnets.**—In Table 5 the number and the dimensions of the magnets are given, together with their magnetic data, determined by Dr. C. W. Burrows and Mr. R. L. Sanford. The quantity, K, appearing in this table is a double ratio—the ratio of the length of the magnet to its cross section divided by the ratio of the length of the air gap to its cross section.

Heinrich and Bercovitz [8] divide this ratio by 100 and call that the factor of safety against demagnetization. This is purely a geometrical quantity and of course does not take into consideration either the composition, the temper, or the flux density of the steel. It is of use, however, in estimating the probable permanence of a magnet and in pointing out radical defects of magnet design.

13. **Miscellaneous Details.**—Figs. 7 and 8 are photographs of all the types of meters with and without covers, while Fig. 6 is a photograph of the moving elements and magnets. Various details of construction in the meters deserve special mention.

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[8] Heinrich und Bercovitz: Handbuch der Electrotechnik [5th ed.], 2, p. 29. Circular 20, Bureau of Standards, p. 17.

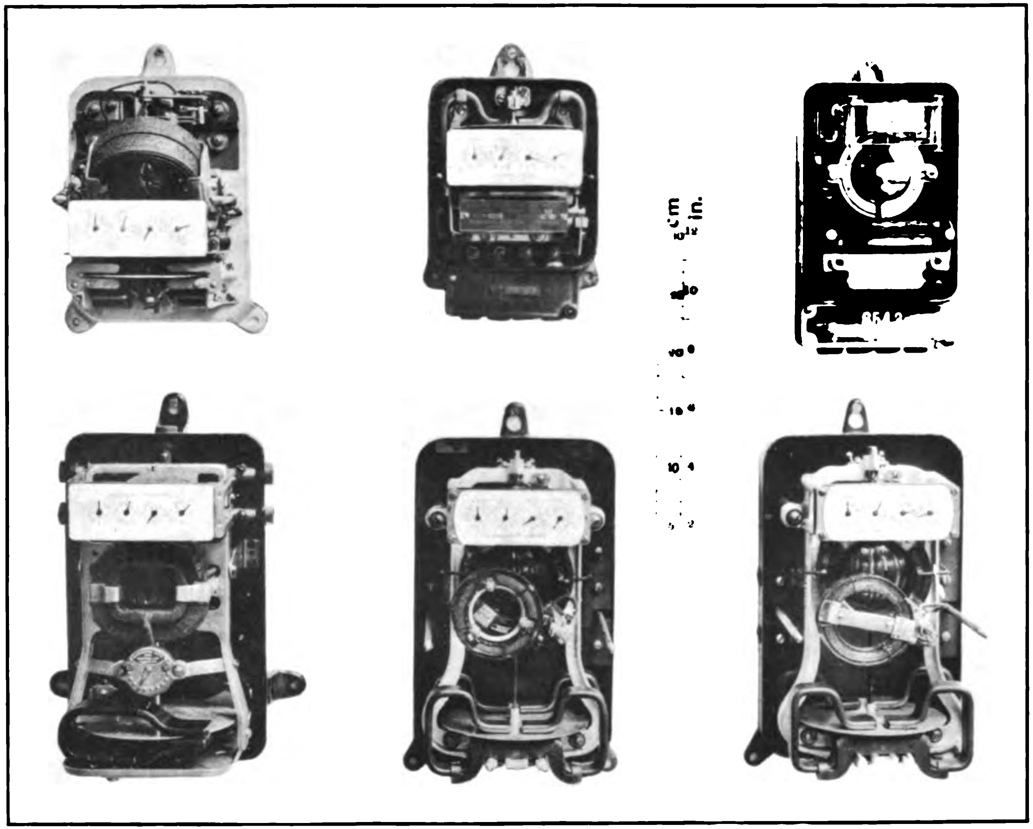

Fig. 8.—*Meters with covers removed*

The armatures of meters A, B, C, E, and F rotate from left to right, while that of D rotates from right to left. It is certainly unfortunate that all watthour meters, both direct current and alternating current, as well as ampere-hour meters, have not been designed to have the same direction of rotation. But since we do not have uniformity in this matter it seems but reasonable that the direction of rotation should be indicated by an arrow on every meter. Meters A, D, and F are so marked.

The spot on the disk should be large enough to be easily seen and should extend over the edge and along the bottom of the disk. While it is a mere detail, it would be a convenience in testing if this spot were located on the same radial line as the set screw of the disk. This would avoid the confusion which may arise at the higher speeds, and the spot could then be used at the beginning and the end of a run to secure greater accuracy. None of these meters were so arranged.

Meters A, D, and F have special arrangements for easily removing the dials for checking gear ratio; in meter F, however, this results in freeing the upper pivot. Meter F has a cyclometer dial with a device for equalizing the friction load on the armature. Meters B and F have special devices designed to render the covers more easily removed and replaced. Meters A, B, D, and F allow observation of the disk when the cover is on.

Meters A, D, and F have micrometer adjustments of the drag magnets for regulating the rate of the meter. Meters E and F use a steel ball and two jewels instead of a pivot and jewel bearing. Meters A, C, and E are provided with springs to take the weight of the moving element off the jewel when the meter is to be moved.

IV. DISCUSSION OF FRICTION LOSSES AND THEIR EFFECT UPON THE LOAD CURVES

14. **Separation of Friction Losses.**—There are four principal sources of friction in a watthour meter, the brushes, bearings, gearing, and windage. Few attempts have been made to determine the magnitude of these losses separately and to study their effect on meter performance. Schmiedel,[9] however, has published a systematic investigation on this subject in which he gives a large number of

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[9] Schmiedel, Verhandlung des Vereins zur Beförderung des Gewerbfleisses, Vols. 89-90, 1910-11. The Electrical Review, (London) **69**, Dec. 22, 1911. Science Abstracts.

curves for the different losses both in alternating-current and direct-current meters.

To determine the frictional losses it is necessary to remove the drag magnets, as they produce most of the retarding torque, compared with which the friction torque is small. In physical measurements, other things being equal, the most direct method of measurement is to be preferred. Measurement of the power input for a given speed gives the torque directly in terms of the full-load torque, so from the standpoint of directness it is the best method. The difficulty with it arises from the flatness of the speed-torque curve over a considerable range of speeds, which causes the meter to run in a state of indifferent equilibrium. This method was used only as a check except for meter D, which has large fluid friction due to the mercury.

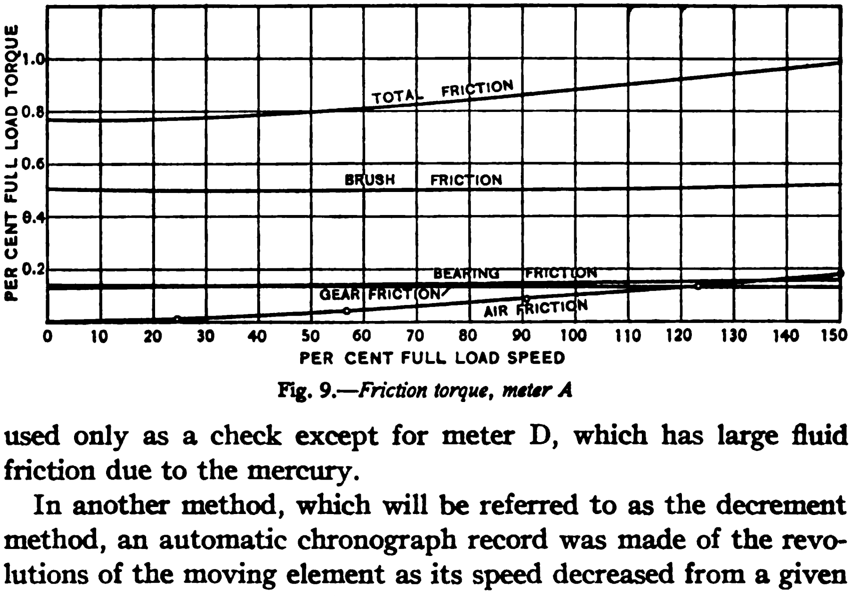

Fig. 9.—*Friction torque, meter A*

In another method, which will be referred to as the decrement method, an automatic chronograph record was made of the revolutions of the moving element as its speed decreased from a given initial value to zero. From this record and the moment of inertia of the moving element the torque was calculated. In obtaining the chronograph record a transformer of small capacity giving about 3000 volts was arranged so that at each revolution of the moving element a spark was drawn from a rider on the disk to one high-tension terminal, the other terminal being grounded on the frame. Only the primary current of the transformer drawn at 120 volts was passed through the operating coil of the chronograph. An incandescent lamp in this circuit limited the current.

This arrangement gave automatic operation of the whole mechanism for getting the data of the revolution-time curves, while the torque introduced by the arc is inappreciable. The record of normal running of a meter shown in Fig. 3 was obtained by this method. This method of timing meters has been developed independently and described in detail by Thompson.[10] The speed-torque curves for the brush, bearing, and gear friction shown in Figs. 9 to 14, inclusive, were determined by this method. To get these values it was necessary to take chronograph records as described, first with brushes and gear train on, then with brushes off and gear on, and finally with both brushes and gear off. The last of these gives the windage and bearing friction, and the gear

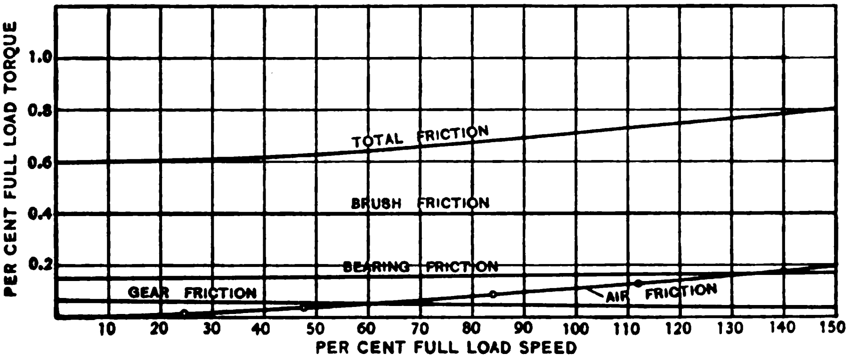

Fig. 10.—*Friction torque, meter B*

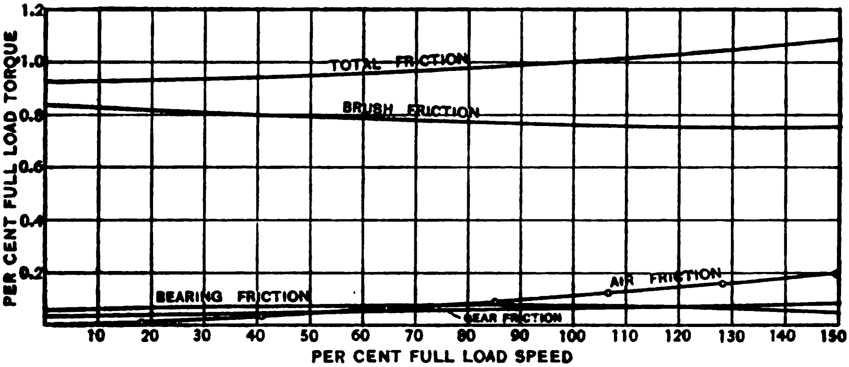

Fig. 11.—*Friction torque, meter C*

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[10] Thompson: Electrical World, 61, p. 246; 1913.

and brush friction are obtained by taking differences. The air friction might be separated from the bearing friction in a similar manner by taking runs in a vacuum, but as the difficulties of this test are considerable, another method for getting the air friction was adopted. The drag of the air may be measured by suspending the moving element by a metal strip and rotating the case around it. As it was not convenient to use the cases of the meters, a box having approximately the same shape and giving about the same conditions as the case was used instead, except for meter B, where both case and box were tried. As the results agreed closely for this meter, the box arrangement was deemed a sufficient approximation for the other meters. With the case revolving at a given speed the angle of torsion of the moving element was read off by means of a mirror with telescope and scale. The torque of the suspension strip per unit angle of twist was determined by obtaining the period of vibration with a disk of known moment of inertia replacing the watthour meter moving element.[11]

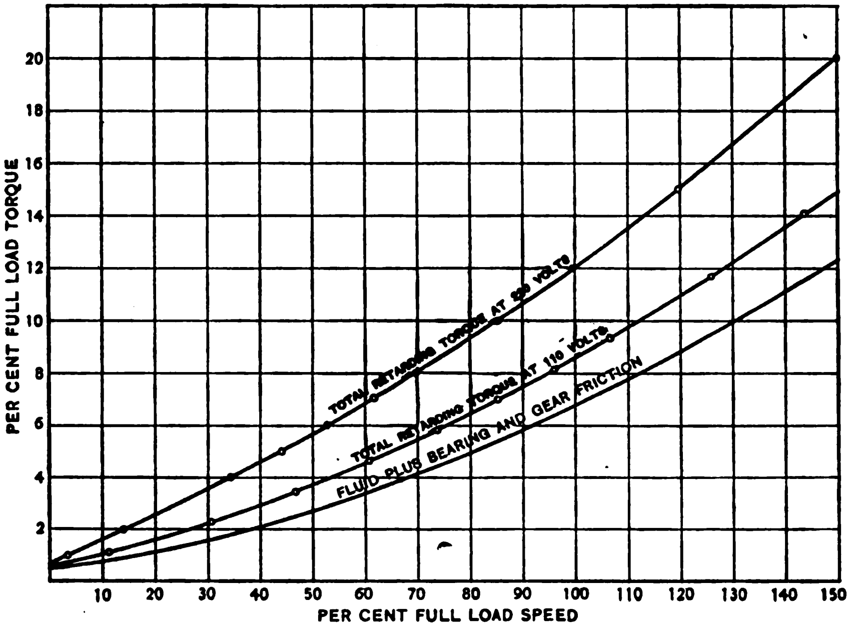

Fig. 12.—*Friction torque, meter D*

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[11] The torque in centimeter-dynes per radian (57°.3) of twist is given by the equation

$$Q=\frac{4\pi^2K}{T^2}$$

where K = moment of inertia in cgs units and T = period of vibration in seconds.

In Fig. 15 are given curves obtained by the decrement method with meter C to determine the retarding effect of the current in the current element. From these curves, which were taken with both brushes and gear off, it is seen that this retarding torque due to the current is comparable in magnitude with the bearing-friction torque. After replacing the steel shaft by an aluminum one this effect was found to have practically disappeared. Meter A

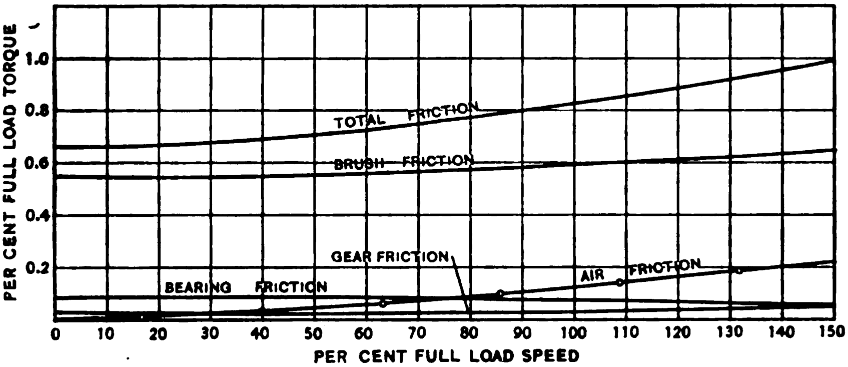

Fig. 13.—*Friction torque, meter E*

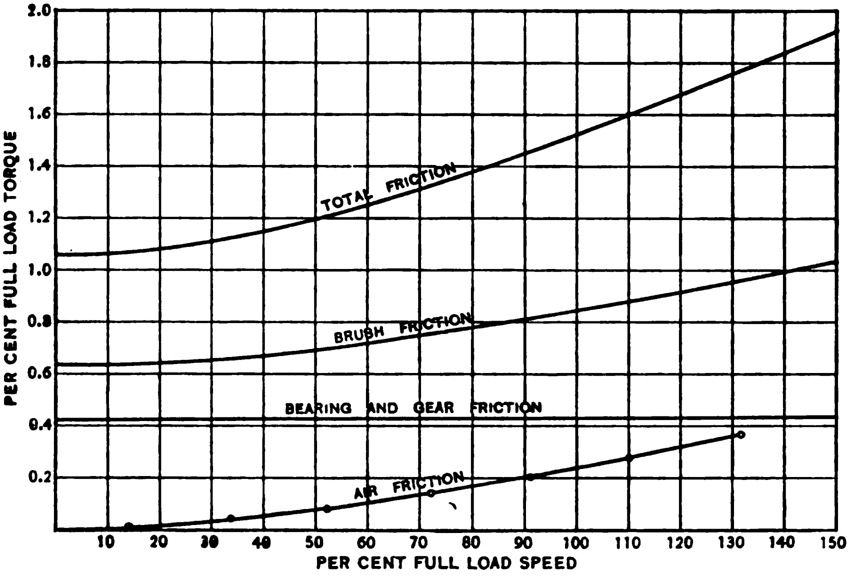

Fig. 14.—*Friction torque, meter F*

showed a similar effect, though it has a brass shaft, but in this instance it appeared to be due to the drag action of the flux from the series coil on the disk itself, which is close to the current element in this meter.

To get the value of the friction torque from the chronograph records it was necessary to analyze the revolution-time curves, some typical examples of which are given in Fig. 16. By changing the algebraic sign of the time the revolution-time curve may be plotted with the instant of stopping as the zero of time. The curves of Fig. 17 were plotted in this way. The advantage of plotting the curves backwards is that the mathematical treatment of the problem is much simplified. The following set of symbols will be used in this discussion:

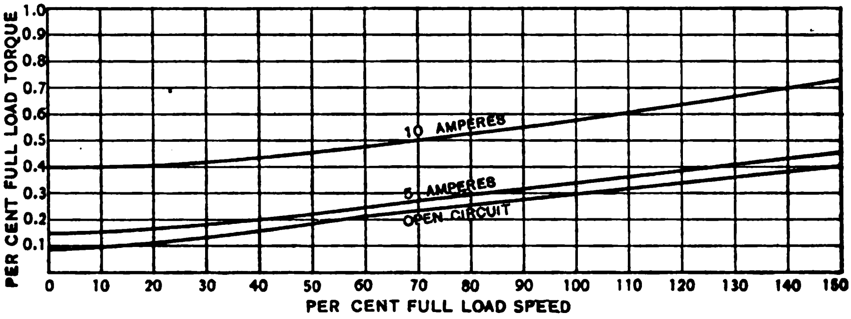

Fig. 15.—*Friction torque, showing effect of current in series coils*

K = moment of inertia.
Q = torque.
θ = angle of rotation.
N = number of revolutions.
t = time.
R = resistance.
ϕ = flux.
E = voltage.
I = current.
ω = angular velocity.
a, b, c, and d = constants.

Considering the curve to be plotted as if the speed were increasing instead of decreasing, and assuming the friction torque to be constant, we may write the differential equation of motion:

$$K\frac{d^2\theta}{dt^2}=Q \qquad (1)$$

Integrating:

$$K\frac{d\theta}{dt}=Qt+c_1$$

$$K\theta=\frac{1}{2}Qt^2+c_1t+c_2$$

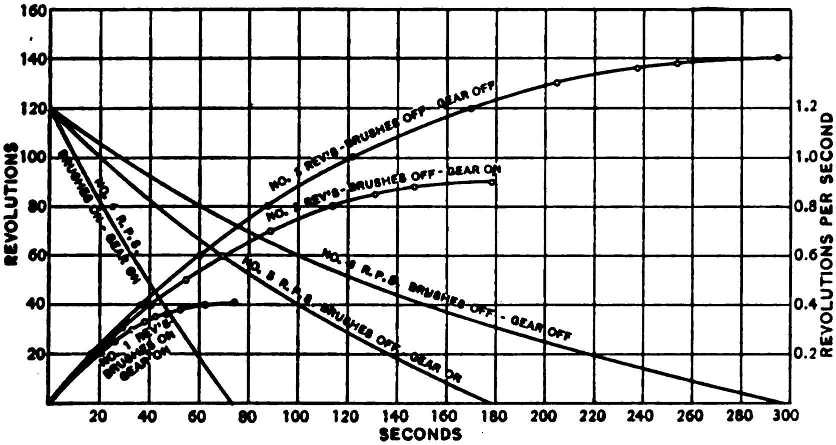

Fig. 16.—Nos. 1, 2, 3, revolution-time curves; Nos. 4, 5, 6, speed-time curves corresponding

When $t=0, \theta=0$ and $\frac{d\theta}{dt}=0$,

since the meter is supposed to start from rest.

$$\therefore c_1=c_2=0$$

We have then as the algebraic equation of motion,

$$K\theta=\frac{1}{2}Qt^2$$

or

$$\theta=\frac{1}{2}\frac{Q}{K}t^2=ct^2 \qquad (2)$$

This is the equation of a parabola, but it was found that it does not fit the retardation curves. Various assumptions might be made in writing the differential equation of motion instead of assuming the friction torque to be constant, as was done above. But as it is not known just what assumptions to make, it appears better to assume N as a function of t in the first place, guided by the result in the simple case where the friction torque is assumed to be a constant. The simplest assumption to make is a power series:

$$N = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + \dots \qquad (3)$$

The curves as actually taken are for retarded motion; but if a curve were to be taken with accelerated motion—as, for instance, by putting on a driving torque varying in such a way that it would be at all times twice the retarding torque—there appears to be no reason for supposing that the shape of the revolution-time curve would be different. That is, N would have the same absolute value for the same absolute value of t positive or negative. In other words, N is a function of the even powers of t as shown in Fig. 18.

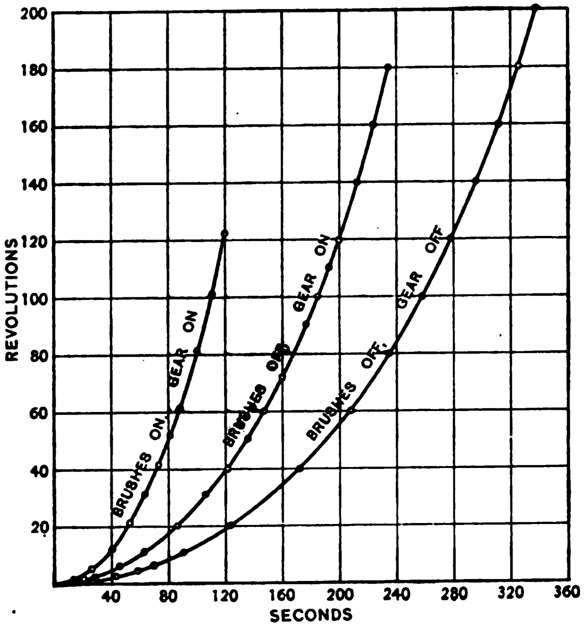

Fig. 17—*Revolution-time curves plotted backwards*

This eliminates odd powers of t. With these assumptions the equation may be written

$$N = at^2 + bt^4 \tag{4}$$

neglecting all powers of t above the fourth. This equation was found to fit the revolution-time curves of all the electrodynamometer meters with close approximation.

To get the values of a and b for any given curve, it is necessary to solve two simultaneous equations:

$$\left.\begin{aligned} N_1 &= at_1^2 + bt_1^4 \\ N_2 &= at_2^2 + bt_2^4 \end{aligned}\right\} \tag{5}$$

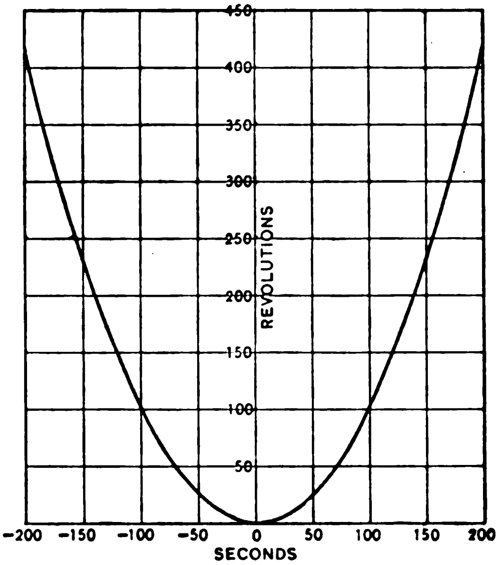

Fig. 18.—*Revolution-time curve. Plot of equation* $N=at^2+bt^4$ *where* $a=10^{-2}$, $b=10^{-8}$

Solving:

$$\left.\begin{aligned} a &= \frac{N_1t_2^4 - N_2t_1^4}{t_1^2t_2^4 - t_1^4t_2^2} \\ b &= \frac{N_2t_1^2 - N_1t_2^2}{t_1^2t_2^4 - t_1^4t_2^2} \end{aligned}\right\} \tag{6}$$

Before making the solution as above, an approximate solution was first made for very small values of the time, where the fourth-power term is negligible in comparison with the square term. This gives the fraction of a turn at the beginning of the run and the time corresponding to it. These quantities are usually determined from the first three whole turns of the speed-time curve as here considered, actually the last three whole turns of the meter before stopping.

Assume:

$$\begin{aligned} N_1 + x &= a(t_1 + y)^2 \\ N_2 + x &= a(t_2 + y)^2 \\ N_3 + x &= a(t_3 + y)^2 \end{aligned} \qquad (7)$$

Where x is the last fraction of a turn and y the time taken for it.

Solving:

$$\begin{aligned} y &= \frac{(N_3 - N_2)\ (t_2^2 - t_1^2) - (N_2 - N_1)\ (t_3^2 - t_2^2)}{2\left[(N_2 - N_1)\ (t_3 - t_2) - (N_3 - N_2)\ (t_2 - t_1)\right]} \\ a &= \frac{N_2 - N_1}{t_2^2 - t_1^2 + 2y(t_2 - t_1)} \\ x &= a(t_1 + y)^2 - N_1 \end{aligned} \qquad (8)$$

In some cases the values of x and y were measured; that is, the disk was watched as it was stopping and a punch made on the chronograph sheet by hand at the instant of stopping. When the disk was accurately leveled to avoid the effects of unbalancing, the measured values checked closely with those computed.

Having these correction terms for the turns and time, respectively, a solution can be made according to equations (5) and (6), giving the constants in the equation:

$$N = at^2 + bt^4.$$

The first derivative of this equation gives the speed in revolutions per second:

$$\frac{dN}{dt} = 2at + 4bt^3 \qquad (9)$$

The second derivative multiplied by 2π gives the angular acceleration in radians per second per second, or the torque is given by the equation:

$$\begin{aligned} Q &= K\frac{d^2\theta}{dt^2} = 2\pi K\frac{d^2N}{dt^2} \\ &= 2\pi K(2a + 12bt^2) \qquad cm - dynes \qquad (10) \\ &= \frac{2\pi K}{981}(2a + 12bt^2) \qquad cm - g \end{aligned}$$

Equations (9) and (10) give the necessary data for plotting the speed-torque curves.

Owing to the relatively large amount of fluid friction of the mercury meter D, the method of getting the friction torque from speed-time curves was not very successful. The rotating element, under this viscous damping only, will stop in 6 or 7 revolutions after being set in motion at twice full-load speed. The friction torque of this meter was obtained by running it as a watt-hour meter, but with magnets removed. Two speed-torque curves were taken in this way, one at 220 volts and the other at 110 volts. For the same value of ϕI—that is, for the same torque—there is a marked difference in speed at the two voltages. This is due to the difference in the damping caused by the flux from the potential circuit winding, which cuts the driving disk in the mercury chamber. From these two curves the viscous damping plus bearing and gear friction was deduced. This was done on the assumption that the magnetic drag is proportional to the square of the flux. The ratio of the flux at 110 to that at 220 volts was obtained by measuring the torque, first at 10 amperes 220 volts and then with 20 amperes 110 volts. From these values the amount of magnetic drag at 110 volts was computed for each point and a subtraction made giving the curve of total friction. (See Fig. 12.)

TABLE 6

Components of Torque

Torque	Unit	A	B	C	D	E	F
Brush friction	cm-g	0.038	0.057	0.127	....	0.090	0.024
	Per cent full load	.50	.40	.76	....	.60	.84
Gear friction	cm-g	.010	.006	.010	....	.004	....
	Per cent full load	.13	.04	.06	....	.03	....
Bearing friction	cm-g	011	.023	.013	....	.012	.013
	Per cent full load	.15	.16	.08	....	.08	.44
Air friction	cm-g	007	.016	.018	....	.019	.007
	Per cent full load	.10	.11	.11	....	.13	.44
Total friction	cm-g	.066	.102	.168	0.216	.125	.044
	Per cent full load	.88	.71	1.01	[12] 5.50	.84	1.52
Drag magnet	cm-g	7.40	14.21	16.52	3.70	14.80	2.81
	Per cent full load	99.12	99.29	98.99	94.50	99.16	98.48
Full load	cm-g	7.47	14.31	16.69	3.92	14.92	2.85

[12] Mostly liquid friction torque which partly replaces the retarding torque of the drag magnets.

The curves of Figs. 9 to 14 show the results of the work in separating the friction torques for one meter of each type. While the experimental difficulties are considerable, it is believed that the curves not only give the correct order of magnitude but that they are fair approximations to the actual quantities. As the friction forces, air friction excepted, vary from time to time, very accurate measurements would be of little value even if attainable. The general results are in good agreement with those of Schmiedel. From the curves given it appears that the air friction is probably responsible for nearly all the curvature in the curves for total friction torque. In the only curves given by Schmiedel for air friction torque alone, he shows them as straight lines; but it is possible that he considered the accuracy of determination of those particular curves was not sufficient to give the departure from a straight line. The friction torques due to the brushes, the gearing, and the bearings are constant within experimental error.

It should be stated that the brush friction, which in each instance constitutes more than half the total, does not depend on the type of meter alone, but depends in large measure upon the adjustment of brush pressure for each individual meter. Hence the data as given here on single meters can not be used to compare the different types.

15. **Discussion of Load Curves.**—The common explanation of the shape of the load curve of the commutator type of direct-current motor meters is that the rise in the curve between light load and full load is due to the increase in friction at lower speeds and that the droop at overload is due to the back electromotive force in the armature. Measurements of the back electromotive force show it to be inadequate to explain this droop, as may be seen by reference to table 1, which shows the largest value to be only 0.19 volt.

The explanation mentioned is not only superficial but is actually misleading, as it seems to demand that the curve of total friction should pass through a minimum, which will be shown to be unnecessary. There is some indication that at low speeds the curve of total friction torque passes through a slight minimum which the curves as drawn do not show. If a meter with the magnets removed is driven as a watthour meter, it will not run steadily below 15 or 20 per cent of full-load speed. In other words, this is a region of instability of running. This would be a natural result if the friction torque curve has a slight minimum at low speeds, since for stable running it is evidently necessary that the retarding force should increase with the speed—a condition always fulfilled when the magnets are on, at least within the range of working speeds.

The electrodynamic load curve will be considered first; that is, the curve as it would be were there no heating effects from the current in the series coils. Let AB in Fig. 19 represent the total friction torque curve. Draw the straight line A′ B′ through the values of the torque at 10 per cent and 100 per cent speed. If the starting torque were made to compensate for the friction at the 10 per cent point and if the friction increased directly as the speed, or, in other words, followed a linear law such as indicated by the straight line A′ B′, the speed of the meter would be proportional to the driving torque. That is, the friction torque could be added in as part of the retarding torque and would follow the same law as the retarding torque due to the magnets. As the retarding friction torque actually follows a curve concave upward, its value is too great below 10 per cent load, too small

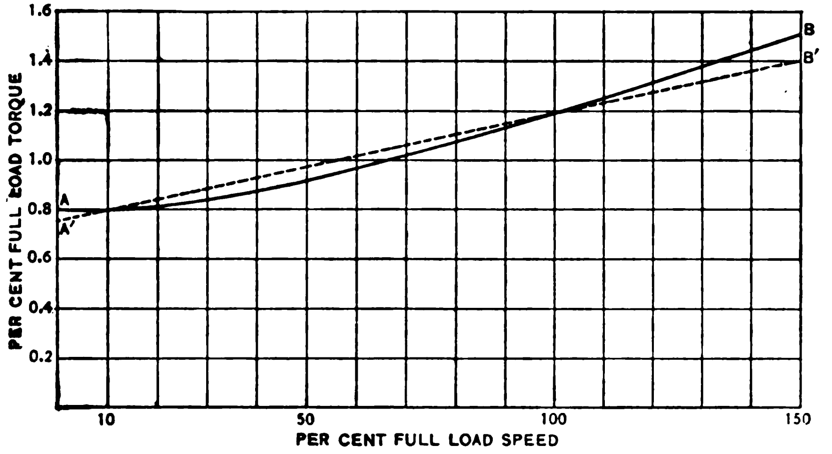

Fig. 19.

for loads between 10 per cent and 100 per cent, and too great above 100 per cent load. The meter as a consequence tends to run slow at less than 10 per cent load, fast between 10 per cent and full load, and slow at overloads. All this depends on the assumption that the meter is adjusted to be correct at the 10 per cent and full load points, though the general kind of deformation of the load curve would be the same whatever the adjustment. Applying this theory to the actual friction curves of the meters it is found that, taken together with the back electromotive force, it practically accounts for the shape of the electrodynamic load curve.

The driving torque Q_d may be analytically expressed in the form:

$$Q_d = C_d + DI\left(\frac{E - a\omega}{R}\right) = C_d + D_1 I - D_2 I\omega \qquad (11)$$

where the constant C_d represents the starting torque of the light-load adjustment, I the load current, E the impressed voltage, $a\omega$ the back electromotive force, which is proportional to the speed ω, R the potential circuit resistance, and D, D_1 and D_2 proportionality constants. In a similar way the retarding torque may be expressed in the form of a series, omitting terms greater than the square:

$$Q_r = C_r + D_3\omega + D_4\omega^2 \qquad (12)$$

where C_r is the initial value of the friction torque, $D_3\omega$ the retarding torque of the drag magnets, and $D_4\omega^2$ represents the change in friction torque with speed.

For the condition of running:

$$Q_d = Q_r$$

Subtracting (12) from (11) gives:

$$C_d - C_r + D_1 I - D_2 I\omega - D_3\omega - D_4\omega^2 = O$$

Solving:

$$\omega = \frac{1}{D_3}(C_d - C_r + D_1 I - D_2 I\omega - D_4\omega^2) \qquad (13)$$

Since $D_2I\omega$ and $D_4\omega^2$ are only small correction terms they may be replaced by their approximate values D'_2I^2 and D'_4I^2, respectively, assuming the speed to be proportional to the current.

Substituting these values in (13) gives:

$$\omega = \frac{1}{D_3}[C_d - C_r + D_1I - (D'_2 + D'_4)I^2] \tag{14}$$

If the meter does not creep at no-load:

$$C_r > C_d$$

Equation (14) may then be rewritten:

$$\omega = -C_0 + C_1I - C_2I^2$$

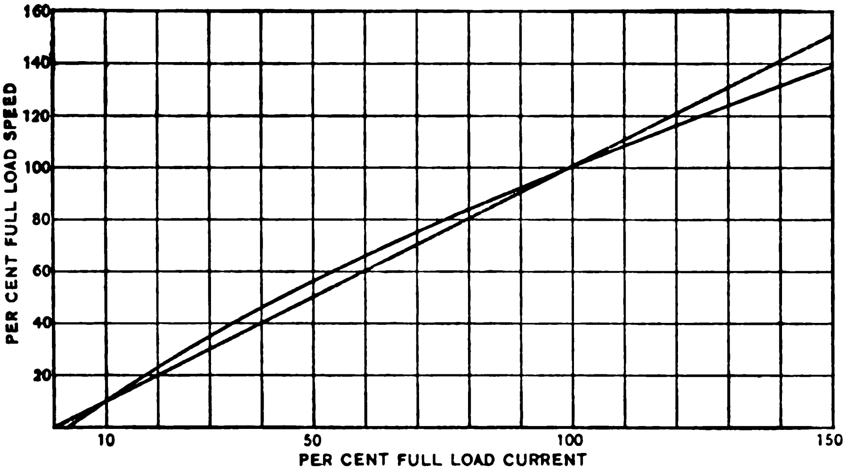

Fig. 20.—*Speed-current curve, showing variation from a straight line*

The negative sign is chosen for C_0 to indicate that under the assumed conditions the meter will not start until some small value of the line current is attained. The term involving I^2 is very small, amounting to only three or four thousandths of the term involving I even at the largest values of the current. Figure 20 represents graphically the variation of angular velocity with current in the series coils according to equation (15). A straight line may be drawn through the zero cutting the curve in two points and so the ratio of the velocity to the current is the same for these two points.

The significance of this is that a meter may be adjusted to be correct at two loads only. The departure of the curve from the straight line, as drawn, is greatly exaggerated.

The dotted lines of Fig. 1 show the effect of heating of the series coils upon the load curve.[13]

The reason for the unavoidable increase in the rise of these curves between 10 per cent and full load can now be understood. In an ideal meter where there would be no heating, the load curve would be the electrodynamic curve *AB* of Fig. 21. In the actual meter the current coils have resistance, and as the heating is proportional to the square of the current, the meter rate is reduced much more at the higher loads than at lower, so that the curve *AB* changes into *AC*. The curve *AC* may now be shifted parallel to itself by the full-load adjustment until it takes the position *DGE*, such that when the 10 per cent load point is made correct, the full-load point will be correct. The point *D* is made to coincide with *A* by changing the friction compensation. The curve will now have the position *AHF*, showing the meter to be

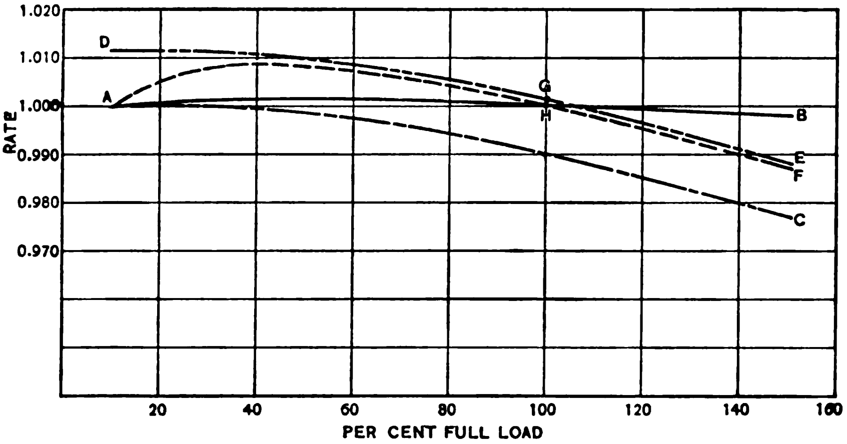

Fig. 21.—*Effect of heating of series coils*

correct at 10 per cent and full load but running fast at intermediate loads where the effect of light-load compensation and heating are both small.

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[13] The heat developed in the series coils causes the resistance of both armature and disk to be increased. The increase of armature resistance causes a decrease in driving torque with a corresponding decrease in the rate of the meter. The increase of the resistance of the disk causes a decrease in retarding torque, but as the disk is located at a greater distance from the source of heat than the armature the changes in these torques do not balance.

An examination of the various load curves in Figs. 1 and 2 shows that the heating effect of the series coils is the chief factor in determining the shape of the load curves, as the deformations due to it are greater than those due to the friction and back electromotive force.

We are indebted to Dr. P. G. Agnew for many valuable suggestions in connection with this work.

V. SUMMARY

1. A large amount of numerical data is given in regard to the performance and construction of six types of American meters. (See Tables 1 to 5, pp. 165, 166, 170, 171.)

2. The total friction torque is separated into four parts—brush, gearing, bearing, and windage friction—and curves are plotted of these components of torque against speed. A description is given of the method used in obtaining these curves. (See Table 6, p. 183.)

3. The load curve is analyzed and its shape is shown to depend upon the heating of the series element, the variation in the friction torque, and the back electromotive force.

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WASHINGTON, July 11, 1913.

WINDAGE RESISTANCE OF STEAM-TURBINE WHEELS

A CRITICAL STUDY OF THE EXPERIMENTAL DATA WHICH HAVE BEEN PUBLISHED AND OF EQUATIONS FOR REPRESENTING THEM

By E. Buckingham

1. *General Considerations.*—The power dissipated in driving a given wheel against the resistance of the surrounding medium, depends on the speed of rotation and the mechanical properties of the medium.

If the medium is an homogeneous fluid such as water, air, or dry steam, its mechanical behavior is determined by its density, viscosity, and compressibility. If the linear speeds involved are all small compared with the speed of sound in the medium, the energy of the acoustic waves generated is insignificant, the drag on the wheel due to the generation of these waves is negligible, and the medium acts sensibly as if they did not exist, i. e., as if it were incompressible. Except possibly in extreme cases, it can hardly be doubted that treating the medium as incompressible is allowable to the degree of approximation needed in steam-turbine calculations or justified by the accuracy of published determinations of windage losses. The density and viscosity of the medium in which the wheel rotates are therefore the only ones of its physical properties which we need to take into account, so long as the medium is homogeneous.

If instead of confining our attention to a particular wheel and casing we extend it to other wheels of various sizes which are, together with their casings, geometrically similar to the wheel and casing first considered, we see that the power dissipated may, further, depend on the diameter of the wheel, this single magnitude sufficing for the complete geometrical specification of the system when the shape is once given. The shape itself may be specified by the values of the ratios of a number of lengths to some one length, such as the diameter of the wheel. It is to be understood, in what follows, that when we speak of wheels of the same shape, or "geometrically similar wheels," the similarity is to extend to the casings as well as to the wheels proper.

Let P be the power dissipated in driving a wheel of given shape and of diameter D, at a speed of n revolutions per unit time in an homogeneous medium of density ρ and viscosity μ. Then since the power can depend only on the size of the wheel, its speed of rotation, and the properties of the medium we have

$$P = f\ (\rho, n, D, \mu)$$

This physical equation must consist of terms which are all of the same dimensions, and this can be true only if the equation is of the general form

$$P = \Sigma N \rho^{\alpha} n^{\beta} D^{\gamma} \mu^{\delta} \tag{1}$$

in which the N's are pure numbers and the α, β, γ, δ, of each term have a set of values which give that term the same dimensions as P. There may be any number of terms, but for each of them a dimensional equation,

$$[P] = [\rho^{\alpha} n^{\beta} D^{\gamma} \mu^{\delta}] \tag{2}$$

must be satisfied.

It is most convenient to use the ordinary m, l, t system of fundamental units. If we do so and derive our other units from them, we have the following dimensional equations for the quantities which appear in equation (1):

$$\begin{aligned}[P] &= [ml^2t^{-3}]\\ [\rho] &= [ml^{-3}]\\ [n] &= [t^{-1}]\\ [D] &= [l]\\ [\mu] &= [ml^{-1}t^{-1}]\end{aligned}$$

The exponents of each term in equation (1) must therefore be such as to satisfy a dimensional equation

$$[ml^2t^{-3}] = [m^{\alpha}l^{-3\alpha}t^{-\beta}l^{\gamma}m^{\delta}l^{-\delta}t^{-\delta}]$$

The units of *m*, *l*, and *t* being independent, this equation must be homogeneous in each of them, so that we have

$$\left.\begin{aligned} 1 &= \alpha + \delta \\ 2 &= -3\alpha + \gamma - \delta \\ 3 &= \beta + \delta \end{aligned}\right\} \text{ whence } \left\{\begin{aligned} \alpha &= 1 - \delta \\ \beta &= 3 - \delta \\ \gamma &= 5 - 2\delta \end{aligned}\right.$$

as the relations which must exist between the exponents of each term of equation (1).

If we substitute the foregoing values of α, β, and γ, in equation (1) and take out the common factor $(\rho n^3 D^5)$, we have

$$P = \rho n^3 D^5 \Sigma N \left(\frac{\mu}{\rho n D^2}\right)^{\delta} \tag{3}$$

The number of terms, the coefficient N of each term, and the exponent δ with which the single variable $\left(\frac{\mu}{\rho n D^2}\right)$ appears in that term, all remain indeterminate, i. e., they may have any values whatever without violating the dimensional requirements. We may also write equation (3) in the simpler form

$$P = \rho n^3 D^5 \varphi \left(\frac{\mu}{\rho n D^2}\right) \tag{4}$$

where φ is an unknown function of $\left(\frac{\mu}{\rho n D^2}\right)$.

For wheels of any given shape, the form of the function φ is fixed, but for any other shape the form of φ will or may be different. It depends on the values of a number of ratios of lengths sufficient to fix the shape of the wheel and casing, including the closeness of the casing to the wheel as part of the "shape." These ratios determine the values of the N's and δ's of equation (3). The variable $\left(\frac{\mu}{\rho n D^2}\right)$ has no dimensions, so that its numerical value in any absolute units is fixed by the physical magnitudes of μ, ρ, n, and D, and is independent of the magnitudes of the fundamental units.

2. *Remarks on the Function φ.*—Equations (3) and (4) contain all the information obtainable from the principle of dimensional homogeneity, and further information must be sought elsewhere.

The resistance offered by a fluid to a solid body in steady motion through it may be looked upon as a retarding drag due to transverse communication of momentum between currents or layers of the fluid which are moving over each other with different average velocities and are maintained by the motion of the solid body. In quiet stream-line motion, this transfer of momentum takes place by intermixing on a molecular scale, i. e., by interdiffusion of the different streams of fluid; and the coefficient of viscosity, μ, is a measure of the activity of this molecular intermixing. But whenever, by reason of high speed or of roughness or irregularity of the solid, the motion of the fluid becomes very turbulent, the lateral transfer of momentum between different streams occurs mainly by motions of relatively large masses of fluid in all sorts of irregular cross-currents and eddies. For any given geometrical arrangement of such a state of turbulent motion, this molar transfer of momentum is evidently proportional to the masses involved, or in other words, to the density of the fluid.

We must therefore expect that when the motion of the fluid about the solid body is perfectly quiet and regular, which will usually mean that all the motions are slow, the resistance encountered by the solid will be directly proportional to the viscosity of the fluid. But if, on the other hand, the circumstances are such that the motion of the fluid is very turbulent, it is to be expected that density will play the determining part in the phenomena of resistance, viscosity being of relatively small or even vanishing importance. The substantial correctness of this general qualitative reasoning is established by well-known facts relating to skin friction, aeroplane and ship resistance, and the flow of liquids and gases through pipes. Let us now see what it leads to in connection with equation (3).

If we have to deal with a smooth disk at a low speed of rotation, we must expect the retarding torque and therefore the power absorbed at any given speed to be directly proportional to the viscosity of the medium about the disk. This requires that the second member of equation (3) shall consist of only a single term and that its exponent shall be $\delta = 1$. The equation for the power thus reduces to the very simple form

$$P = Nn^2D^3\mu \qquad (5)$$

and the retarding torque is therefore independent of the density and proportional to the speed of rotation, the viscosity of the medium, and the cube of the diameter of the disk.

If the speed of rotation is increased, the stream-line motion will become unstable and will break up, at or near a certain definite critical speed, into a quite different, turbulent motion. At all events, this is what we should expect from our knowledge of the flow of fluids through pipes, and our expectation is confirmed by experiments on disks. After this abrupt change in the character of the fluid motion, the density of the fluid must appear in any equation which is to describe the facts, and if the viscosity μ appears at all it must be, in each term, with a smaller exponent than that of ρ in the same term. In the limiting case, the viscosity might be of altogether vanishing importance and then equation (3) would necessarily have the form

$$P = N\rho n^3D^5 \qquad (6)$$

the retarding torque being proportional, for a given disk, to the density and the square of the speed, while for disks of different diameters but geometrically similar—in regard to roughness as well as general shape—the torque would be proportional to the fifth power instead of the cube of the linear dimensions. In practice we should expect, rather, that the relation would not reach this very simple limiting form and that μ would still appear, though only in terms with small exponents.

If it is found that the dependence of P on ρ, n, D, or μ can be represented with a degree of approximation sufficient for the experimental accuracy by giving the independent variable a single fixed exponent, it follows that the second member of equation (3) may be represented by a single term, the others being negligible. Equation (3) then reduces to

$$P = N\rho^{1-\delta}n^{3-\delta}D^{5-2\delta}\mu^{\delta} \qquad (7)$$

It appears that such an equation is adequate to the representation of the experimental data which are available—the experimental accuracy not having been high. Equations (5) and (6) correspond to the limiting values $\delta = 1$ and $\delta = 0$.

The value of N depends on the form of the wheel and casing. For a bladeless disk running in the open, it depends on the profile and the roughness. For a thin flat disk it depends on the roughness alone; but the roughness is to be measured in terms of the diameter, so that for a surface with granulations or irregularities of a certain general absolute size, a large disk is "smoother" than a small one, in the present sense of the term smooth.

For smooth plane disks of small thickness, the critical speed, at which stream line motion breaks up into turbulent motion and the exponent δ drops suddenly from nearly unity to a much smaller value, is fairly definite and the change in the law of resistance is sharp. For ordinary turbine wheels, consisting of a disk and blades, the change is less abrupt and there is no definite critical speed; for the motion about the blades must always be turbulent at any speeds which are high enough to be of practical interest. The smaller the ratio, $\frac{l}{D}$, of blade length to disk diameter, the more nearly the behavior of the wheel approaches that of a simple disk, while with long blades, the additional resistance due to the blades is so much greater than that which would be encountered by the disk alone, that although the law of resistance is different at high and at low speeds the change is gradual.

In an experimental study of the form of the function φ we have first to work with wheels of some one shape, preferably a simple one, to start with. If we then find, as in fact we do for considerable ranges of the variables, that the dissipation P is proportional to a fixed power of ρ, or of n, or of D, or of μ, we know that equation (7) is adequate for this shape of wheel and our experiments give us the value of the coefficient N for this shape as well as the value of δ, no matter which of the four variables we may have selected for independent variation during the experiments. There are thus, in principle, four different modes of attacking the problem which must lead to the same result and may be used for checking one another. In practice we can not always conveniently vary the density and viscosity of the medium independently, so that there are often only three modes of attack which are practicable.

The general procedure is obvious; keeping any three of the variables at fixed values, we vary the fourth and observe the corresponding values of P. If the phenomena can be described by equation (7), the values of log P when plotted against the logarithm of the independent variable will give points which lie on a straight line, within the experimental errors. The slope of this line is the exponent with which the independent variable appears in equation (7); it determines the value of δ. The position of the line, taken in connection with the fixed values of the other three variables, determines the value of N. We may now proceed to examine the experimental data which illustrate the foregoing statements. Readers who are interested only in the final result of this somewhat laborious examination may proceed at once to section 6, page 214.

3. *The Relation of Power Dissipated to Speed of Rotation.*—A. Disks Without Blades: As the simplest sort of wheel we may take a flat bladeless disk rotating in the open air. We have data on such disks from Stodola's[1] experiments on a smooth but unmachined disk of thin boiler plate and from Odell's[2] experiments on paper disks.

Stodola's disk had a diameter of 537 mm or 21.1 inches, and he gives points on a plot of log P against log n only for 1500, 1800 and 2000 r. p. m. These three observations very nearly satisfy the relation $P \propto n^{2.92}$. The retarding torque was thus proportional to the 1.92 power of the speed n, which is about what might have been expected from the work of Reynolds,[3] Froude,[4] Zahm,[5] and others.

Odell's experiments covered a wider range of speed and he used four disks with diameters of 15.0, 21.8, 26.8, and 47.1 inches, recording the torque needed to drive each disk at measured speeds. When log *torque* is plotted against log n it is found that for any given disk, the points for all the higher speeds lie close to a straight line. Upon decreasing the speed, a critical speed, n_c, is reached and the law of resistance changes abruptly.

The results, so far as they concern us at present are collected in Table 1.

TABLE 1

Odell's Experiments on Paper Disks Rotating in Air

	A	B	C	D
Diameter in inches, D=	15.0	21.8	26.8	47.1
Range of speeds, (r. p. m.)	113 2100	200 900	100 525	250 740
Critical speed, n_c=	918	376	243	(100)
Value of β for $n > n_c$	3.32	3.55	3.54	3.08
$10^{-6} n_c D^2$	2.07	1.79	1.75	

The values of n_c and of the speed exponent $\beta = 3 - \delta$ were found by replotting Odell's observations; they do not differ much from Odell's values. The value of β is, of course, obtained by adding unity to the slope of the line on the plot of log *torque* against log n.

Upon inspection of the logarithmic plot there is no doubt that above the critical speed, β is very nearly constant, and there is also no doubt that the values of β are distinctly different for the different disks, the uncertainty in finding β from the published observations being not over 0.1. If the disks had all been geometrically similar, the form of φ in equation (4) would have been the same for all and the exponent β would therefore have had the same value. Since the values of β are not the same, we are sure that the disks were sensibly dissimilar. They were, in fact, made of four different kinds of paper and it could not be expected that they should be either similarly rough or similarly stiff.

When thin paper disks are driven at high speeds they become covered with fluttering waves which must have an important effect in increasing the resistance, so that it is not safe to draw conclusions regarding rigid disks from results obtained with flexible ones. Disk D made of "canvas-backed diagram paper" was no doubt much the stiffest, the others being of two kinds of drawing paper and of cartridge paper. It gave the value $\beta = 3.1$ which is not far from the value 2.92 for Stodola's disk.

Disks B and C gave nearly the same value of β at the high speeds and seem to have behaved as if geometrically similar; the wave systems in them had similar effects on the resistance.

When two geometrically similar wheels or disks are compared, any singular point on the curve $P = f(n)$, such as the critical speed, must by equation (4) occur at the same value of $\frac{\mu}{\rho n D^2}$ for both. In Odell's and Stodola's experiments the medium (air) was always approximately unchanged, so that the value of $n_c D^2$ should be the same for geometrically similar disks. The values in the last line of Table 1 show that this was nearly true for Odell's disks B and C, which gave the same value of β at speeds above the critical. The value of n_c given in the table for disk D was computed from that observed for A which was most nearly like D; it is only a rough approximation, and being far below the lowest speed used with this disk, it was not observed. The critical speed for Stodola's disk, computed in the same way, would be in the vicinity of 500 r. p. m., which is also below the lowest speed recorded.

Disk C, of cartridge paper, shows the interesting phenomenon of two critical speeds, the lower, not mentioned in Table 1, being at about 150 r. p. m. Below this, the torque is proportional to $n^{1.1}$ or, within the experimental errors, directly to n. We have thus the limiting case described by equation (5) or by equation (7) with $\delta = 1$. At the first critical speed it appears that the stream-line motion of the air broke up into turbulent motion, the torque became proportional to $n^{1.7}$ and the power dissipated to $n^{2.7}$. For the range between the two critical speeds we therefore have $\beta = 3 - \delta = 2.7$, $\delta = 0.3$. At the second critical speed of about 243 r. p. m. the disk suddenly began to flutter * and the law of resistance changed to $P \propto n^{3.5}$, a new element being introduced by the presence of waves on the disk. The middle range, between the two critical speeds corresponds to Stodola's observations on his rigid disk. The value $\beta = 2.7$ which is somewhat lower than Stodola's $\beta = 2.92$ indicates that the cartridge paper, as long as it stayed plane, was smoother than the boiler plate, which is not surprising.

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* This is the writer's inference; Odell is not responsible for it.

Disk B shows only the upper critical speed, the observations below this point being very few and the lowest coming about where the lower critical speed would probably have been found. Since the upper critical speed and the phenomena at still higher speeds depend on the stiffness of the disk, which has not appeared at all in our equations, the close agreement of β and of n_cD^2, for disks B and C, must be regarded as in some degree accidental. It happened that the disks were similarly stiff or, at all events, developed wave systems which had similar effects on the resistance.

The few observations on disk B below the upper critical speed give $P \propto n^{2.5}$. We can not say that this is different from the value $\beta = 2.7$ obtained for disk C, the evidence not sufficing to decide the point. But the difference, if real, is in the direction indicated by what we can judge of the smoothness of the two disks as described by Odell. For B was of a smoother thinner drawing paper than A, i. e., probably a rather hard smooth-surfaced paper, while the "cartridge paper" of disk C probably had a somewhat fuzzy surface.

If we compute the critical speeds of the rigid disk D and of Stodola's steel disk from the lower critical speed of disk C, we get 49 and 244 r. p. m., respectively, values about half those computed from disk A and probably nearer the truth.

In the case of disk A, which was relatively stiffer and rougher than B and C, the observations below the single critical speed observed are too scattered for us to detect any lower critical speed, if one occurred, or to distinguish the effects of turbulence of the air and fluttering of the paper. The effect of the fluttering at the high speed was less than with B and C as is shown by the fact that the value $\beta = 3.3$ is nearer the values for rigid disks, e. g., Stodola's disk ($\beta = 2.92$), disk D ($\beta = 3.14$) and disk C between its critical speeds ($\beta = 2.7$). The greater stiffness is also shown by the larger value of n_cD^2; the stiffer disk requires a higher speed to make it break into a flutter.

Odell's experiments were only preliminary and his own opinion of their accuracy is indicated by his saying that $P = const \times n^3D^5$ "agrees pretty well with the experimental results." But in view of the very good agreement which they show with the predictions of the general theory in all cases where the range of speed is large enough, the present writer forms a higher estimate of the interest and relative accuracy of these experimental results, even though the absolute values of the power dissipated may be considerably in error, and though we can evidently not safely predict the behavior of rigid disks from experiments on flexible ones.

B. Ordinary Single-Row Steam-Turbine Wheels: Besides the bladeless disk already mentioned, Stodola experimented on five single-row turbine wheels with various blade lengths and with disk diameters, measured at the root of the blades, of 20 to 45 inches. The wheels were run in air; all of them in the open, and three of them also inclosed in casings. At all the higher speeds the results, as Stodola shows them on a logarithmic plot, satisfy the relation $P \propto n^{\beta}$ quite closely. For the ten series shown, the value of β is from 2.82 to 2.97 with a mean of 2.89 and a mean residual of ± 0.04. The wheels all acted very nearly like the bladeless disk as regards the variation of power with speed.

Lewicki[6] gives the results of a few observations on the windage losses of a small Laval turbine at 14 000 to 20 000 r. p. m. The wheel had a disk diameter of 180 mm or 7.09 inches, and the blades were 20 mm or 0.79 inch long. Three observations in air at atmospheric pressure and 30° C give $P \propto n^{2.43}$ nearly. Four observations in saturated steam at atmospheric pressure lie fairly close to $P \propto n^{3.06}$ while three of them give almost exactly $P \propto n^{3.0}$. There is no doubt that β was nearly constant in each case, but the observations are so few and the range of speeds is so small that no great weight can be given to the numerical values of β.

We have, finally, the results published by Holzwarth.[7] Admitting that for a given wheel running at a given speed in steam, the power dissipated in windage is proportional to the density of the steam, and admitting, further, that for practical purposes the density may be treated as proportional to the absolute pressure p, Holzwarth sets $P = Kp$, and gives the values of K deduced from his experiments, by means of curves on a three-coordinate diagram. Each curve shows the relation of K to n for a given diameter, the diameters being 10, 20, 30, 40, and 50 inches. The lowest speed is 750 r. p. m. and the highest runs up to 4000 r. p. m. for the small wheels. There is a separate diagram for each of the five blade lengths 0.5, 1.0, 1.5, 2.0, and 2.5 inches. The wheels were inclosed but had somewhat more clearance than is usual in practice. No information is given as to how nearly geometrically similar the wheels were, except the mere statement of disk diameter and blade length. The results *appear* to be the most comprehensive we have; but all details are omitted so that we have no means of estimating the accuracy of the experiments, of the reduction of the observations, or of the construction and reproduction of the diagrams as published. Though the curves may be quite adequate to the practical end for which their author intended them, it is evident at a glance that they can not all be represented by a single equation containing only n, D, and l as independent variables, and that readings of K from them are liable to rather large percentage errors.

With the exception of a few curves for the largest diameters and blade lengths, each curve shows two distinct forms and may be divided, though not sharply, into a low-speed and a high-speed part. The relation $K = f(n)$ is different for the two regions and the transition corresponds to the definite critical speed in the case of a bladeless disk. The 10-inch curves fall almost entirely in the low-speed range which is in general of little practical interest. The results for this diameter are therefore omitted from further consideration. For each of the other four diameters the writer made readings of the value of the coefficient K* for each of the five blade lengths and at the various speeds shown on the diagrams. The value of log K was then plotted against that of log n, and 20 series of points were thus obtained, each referring to a fixed diameter and blade length but varying speed.

For the higher speeds, the points of each series lie fairly close to straight lines, sometimes quite close. These lines were drawn in by inspection and their slopes, which represent β in the equation $P = const \times n^{\beta}$ were read off. For the small wheels with short blades there is a fairly definite critical speed at which the relation $P = f(n)$ changes; but the points for the "low" speeds are not exact or numerous enough to show what the relation is at these speeds. For larger wheels or longer blades the transition from "high" to "low" speeds when shown at all is gradual and not sharp, the lowest points on the logarithmic plot being above the straight lines drawn to represent the high-speed points.

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* Holzwarth used the symbol m for this coefficient.

The values obtained for the speed exponent β, are from 2.3 to 3.6; the mean is 3.0 and the mean residual is ± 0.3. The uncertainty of each value, due to doubt as to just where the straight line should be drawn, is generally about ± 0.1 but may be ± 0.2. For most of the series there is no doubt that $P \propto n^{\beta}$ is an approximate representation of Holzwarth's published curves for the higher speeds. There is also no doubt that the values of β, are distinctly different in different cases, but there is no evident systematic variation of the values with either diameter or blade length.

To sum up the conclusions which may legitimately be drawn from the data discussed in the foregoing section, we may say that both for flat bladeless disks and for single-row turbine wheels of ordinary forms, running either inclosed or in the open and in either air or steam, the power dissipated in windage by a given wheel is very nearly proportional to a fixed power of the speed of rotation throughout the range of speeds actually used with the diameters in question, except possibly at the lowest speeds, where the windage losses are economically insignificant. It follows that only a single term need be used in the second member of equation (3), so that an equation of the form (7) or

$$P = N\rho^{1-\delta} n^{3-\delta} D^{5-2\delta} \mu^{\delta} \tag{7}$$

is adequate to representing the facts, over the range mentioned, as closely as we know what the facts are.

The observed values of $3-\delta=\beta$ are grouped about a general mean $\beta=3$ and as a first approximation we have

$$P = N\rho n^3 D^5 \tag{8}$$

the coefficient N having a value determined by the shape of the wheel, and the viscosity not appearing at all. In individual cases the observed values of β vary from 2.5 to 3.5 without our being able to decide, from the rather meagre accounts published, whether the variations are genuine, i. e., not due to errors of measurement, and if they are genuine, what causes them.

The best experiments we have, Stodola's, give $\beta = 2.9$ very nearly, for all of his wheels and all conditions, and this value is quite consistent with the results by other experimenters in similar fields. It is probable that in general the equation

$$P = N\rho^{0.9}n^{2.9}D^{4.8}\mu^{0.1} \tag{9}$$

obtained from (7) by setting $3 - \delta = 2.9$ will give a better approximation than the simpler equation above, in which $\delta = 0$.

At a speed of rotation of 20 000 r. p. m. the peripheral speed of the tips of the blades of Lewicki's wheel was 755 ft. sec. The speed of sound in air at 30° C. is about 1150 ft. sec., and in saturated steam at one atmosphere it is about 1350 ft. sec. The linear speeds which occurred in Lewicki's experiments were therefore by no means all what would commonly be thought of as "small" in comparison with the acoustic speed. Nevertheless, an equation developed on the assumption that compressibility is negligible appears to hold for these high speeds as well as for lower ones. It would have been interesting to have data on the windage of Lewicki's wheel at even higher speeds, for it seems probable that if the speed had been run up to 30 000 the equation $P = const \times n^{\beta}$ would have failed completely. Experiments on the resistance of projectiles[8] indicate that the effects of compressibility begin to be sensible at about three-fourths of the acoustic speed and increase rapidly for some distance beyond that point, so that within a range of from three-fourths to one and one-half times the acoustic speed, the law of resistance is rather complicated. The speeds in Lewicki's experiments appear to have been nearly but not quite high enough to necessitate the consideration of compressibility in making up the theoretical equations. We may conclude that the simple theory as given in section 1 is probably always sufficiently exact when the peripheral speeds are not over one-half the acoustic speed in the medium in question.

4. *The Relation of Power Dissipated to Diameter.*—The experimental results discussed in section 3 suffice to show than an equation of the form (7) describes the facts, and they give us the value of δ in some specific cases. The same information might be got from experiments on geometrically similar wheels, by

making D the only independent variable and comparing the dissipation for wheels of various diameters run at the same speed in the same medium; but no experimental results on exactly similar wheels have been published, so that an investigation by this method can not be based on any published data. Nevertheless, as a check on the previous work it is interesting to compare such imperfect data as we have with equation (7) and the values of δ already found in section 3.

A. Disks Without Blades: We have to select for comparison, disks which gave nearly the same value of $\beta = 3 - \delta$, since disks which do not satisfy this condition can not possibly be geometrically similar. Odell's paper disks B and C gave the same value of β above the fluttering point, but since the rigidity of the disk is here an essential element which has not been allowed for in our theory, we must not expect equation (7) to hold at all exactly. If we compare these disks at 500 r. p. m., the observed power ratio is 4.1 as against 3.5, computed from the diameter ratio and the value $\beta = 3.54$ obtained from the experiments at varying speed. The discrepancy of 15 per cent may be due to experimental error but it seems quite as likely to be due to the fact that the flexibility of the disks has not appeared in the equations.

We may next compare these two disks in the region just below their upper critical speeds, where they were still behaving as if rigid. From the writer's plot of Odell's observations he finds

for disk B $\qquad P = 2.51 \times 10^{-10} n^{2.470}$
for disk C $\qquad P = 2.28 \times 10^{-10} n^{2.654}$

The observations on B in this range are so few that the exponent $\beta = 2.47$ is very uncertain and the equation could not safely be used for extrapolation, but it represents the actual observations reasonably well. At $n = 200$ r. p. m., which is within the range of speeds for both disks, the power computed from these equations is 1.21×10^{-4} hp for B and 2.92×10^{-4} hp for C. Comparing the power ratio with the diameter ratio we have

$$\frac{2.92}{1.21} = \left(\frac{26.8}{21.8}\right)^{4.26}$$

If we regard the disks as similar we have $5-2\delta=4.26$, whence $3-\delta=\beta=2.63$, which is sensibly identical with the value 2.65 obtained directly for disk C.

As a more severe test of the theory we may compare Odell's stiffest disk D, of 47.1 inches diameter, with Stodola's boiler-plate disk of 21.1 inches diameter. At $n=2000$ Stodola observed $P=0.147$ hp and his speed exponent was $\beta=2.92$; hence we have for this disk

$$P=3.38\times10^{-11}n^{2.92}$$

From Odell's measurements on his disk D we have approximately

$$P=48.\times10^{-11}n^{3.08}$$

Odell regarded his experiments on this disk, especially at the lower speeds, as less accurate than his other work, so that it seems only fair to make the comparison at one of the higher speeds within the range used by Odell. Taking $n=700$, we have by the above equations; for Stodola's disk $P=0.00679$ hp, and for Odell's disk D, $P=0.278$ hp. Comparing the power ratio with the diameter ratio we have

$$\frac{0.278}{0.00679}=\left(\frac{47.1}{21.1}\right)^{4.62}=40.9$$

Regarding the disks as similar, we have $5-2\delta=4.62$, whence $3-\delta=2.81$ as compared with $\beta=2.92$, obtained directly for Stodola's disk.

The value $\beta=2.92$ or $5-2\delta=4.84$ would give a power ratio of 48.7. Hence if we use equation (7), with the values of N and δ found for Stodola's disk, to compute the power for Odell's disk at 700 r. p. m. we get within 20 per cent of the observed value. The equation given above for Odell's disk would give, at 2000 r. p. m. and on a diameter of 21.1 inches, $P=0.112$ hp while Stodola's observed value at this speed was 0.147 hp. In view of all the circumstances and the long extrapolation from observations which Odell himself regarded with suspicion, the agreement must be considered quite satisfactory.

B. Single-Row Turbine Wheels: When we look for experiments on geometrically similar turbine wheels we find only a very few cases where we can assume that the wheels were even roughly similar.

One of Stodola's wheels had a disk diameter of 504 mm, or 19.84 inches and a blade length $l = 60$ mm, so that the blade-length ratio was $\frac{l}{D} = 0.119$. This wheel was run in air at atmospheric pressure and temperature, in a casing which allowed an axial clearance of 4 mm at the edge of the blades. Lewicki,[8] as already mentioned, made observations on a Laval wheel which had a disk diameter of 180 mm or 7.089 inches and a blade-length ratio $\frac{l}{D} = 0.111$. These two wheels were therefore nearly similar in respect to the important element $\frac{l}{D}$. From the small scale drawing it appears that Lewicki's wheel had an axial clearance at the blade edges of about 2 mm. For geometrical similarity, the clearance on Stodola's wheel would therefore have had to be about 6 mm instead of the actual 4 mm. Lewicki's wheel thus had relatively more clearance; and since it is known experimentally that reducing the clearance round the blades reduces the windage, we must expect that in making comparisons between the two wheels, Lewicki's observed values will be somewhat larger than values computed for the same speed and diameter from the data obtained by Stodola.

Lewicki's experiments on windage were only a subsidiary part of a larger investigation and are not comprehensive enough to furnish satisfactory values of the constants N and δ. We shall therefore deduce an equation from Stodola's observations and compare values computed from this equation with averages from Lewicki's observations.

The speed exponent given by Stodola for this wheel is 2.87, but it appears from the plot that a larger value might be taken. We can probably do no better than to set $\beta = 2.9$ and use equation (9). At 2100 r. p. m. the dissipation was found to be 0.704 hp.

The disk diameter was 19.84 inches and the density of the air, if we take the value given for the bladeless disk, was $\rho = 1.12$ kgm/m^3 or 0.070 lb./ft.^{3} From these values we get $N\mu^{0.1} = 1.058 \times 10^{-15}$, whence

$$P = 1.06 \times 10^{-15} \rho^{0.9} n^{2.9} D^{4.8} \left(\frac{\mu}{\mu_0}\right)^{0.1} \tag{10}$$

in which

P = the horsepower dissipated.

ρ = the density of the medium in lb./ft.^{3}

n = the speed of rotation in r. p. m.

D = the disk diameter in inches.

μ_0 = the viscosity of the air during Stodola's experiments.

μ = the viscosity of the medium in any other case for which we wish to compute the value of P.

Since most of Lewicki's work was done at a speed of 20 000 r. p. m. we may confine our attention to this speed. If we then set $n = 20\ 000$ and $D = 7.089$, we have

$$P = 38.0 \rho^{0.9} \left(\frac{\mu}{\mu_0}\right)^{0.1} \tag{11}$$

This equation would give us the power dissipated by a wheel geometrically similar to Stodola's wheel but of the same disk diameter as Lewicki's, when running at 20 000 r. p. m. in any homogeneous medium of density ρ and viscosity μ.

To find the correction for the lack of exact similarity, we first make the computation for air because in this case the value of $\left(\frac{\mu}{\mu_0}\right)^{0.1}$ will certainly be sensibly equal to unity. The mean of Lewicki's three observations in air, which do not differ enough to make it worth while to treat them separately, was P(obs) = 4.37 hp at a mean density $\rho = 0.0647$ lb./ft.^{3} Substituting in equation (11) we have P(calc) = 3.24 hp. The ratio $\frac{4.37}{3.24} = 1.35$ indicates that the combined effect of the relatively greater clearance and the slightly smaller blade length of Lewicki's wheel, was to increase the windage loss by about 35 per cent. We therefore modify equation (11) by introducing this correction factor and so obtain, for further use, the equation

$$P = 51.4\rho^{0.8}\left(\frac{\mu}{\mu_0}\right)^{0.1} \tag{12}$$

To compare the values computed by equation (12) with Lewicki's observations in steam we must form an estimate of the value of $\left(\frac{\mu}{\mu_0}\right)$ and it is fortunate that this appears with so small an exponent since we know almost nothing about the viscosity of steam. According to measurements by L. Meyer and O. Schumann (see Landolt and Börnstein's tables) the viscosity of saturated steam at 100° is about 0.72 times that of air at room temperature. We may assume as a sufficient approximation, under the circumstances, that μ is proportional to the square root of the absolute temperature and is independent of the density. In applying equation (12) to steam we therefore have

$$\left(\frac{\mu}{\mu_0}\right)^{0.1} = 0.968\left(\frac{460+t}{672}\right)^{0.05} \tag{13}$$

where t is the temperature of the steam on the Fahrenheit scale. Equation (12) then takes the form

$$P = 49.7\rho^{0.8}\left(\frac{460+t}{672}\right)^{0.05} \tag{14}$$

applicable to dry steam of density ρ lb./ft.^{3} and temperature t °F.

We may first consider the 15 observations made by Lewicki in superheated steam, which was presumably dry and homogeneous though at the lower temperatures this may not have been quite true. The data which concern us are collected in Table 2, reduced to English units.

TABLE 2

Lewicki's Observations in Superheated Steam; n = 20 000 r. p. m.

Pressure p [lb./in.^{2}.]	Temperature t [°F.]	Density ρ [lb./ft.^{3}]	Power P [U. S. hp.]	$\frac{P}{\rho}$	$\frac{P}{\rho^{0.9}}$
14.7	221	0.0368	3.02	82	59
14.7	253	0.0350	2.77	79	57
14.7	406	0.0286	2.33	81	57
14.7	462	0.0268	2.30	86	60
14.7	478	0.0263	2.00	76	53
14.7	531	0.0249	1.98	80	55
14.7	556	0.0243	1.87	77	53
14.7	574	0.0239	1.83	77	53
9.56	586	0.0153	1.08	70	46
5.69	462	0.0100	0.88	88	56
5.69	489	0.0097	0.81	84	52
5.68	259	0.0127	0.94	74	48
5.63	561	0.0089	0.60	69	42
5.39	295	0.0115	0.90	78	50
5.39	590	0.0083	0.58	70	43
Means	448	0.0202		78	52
Mean residuals				±5.8%	±8.5%

The values of the density are not very exact, partly because for the first eight observations the pressure is merely stated to have been atmospheric, and partly because the densities at high superheats are not very accurately known.

In view of the unavoidable errors we can probably do no better than to average the values and set $P = 78\rho$, the mean density being $\rho = 0.0202$ and the mean temperature 448° F. Under these circumstances we therefore have P(obs) = 1.58 hp. Equation (14) with these values of ρ and t gives us P(calc) = 1.51 hp. The agreement of the observed and calculated values to within 5 per cent must be regarded as very satisfactory.

We may also represent the observations fairly well by setting $P(\text{obs}) = 52 \times \rho^{0.9}$, while equation (14) gives us $P(\text{calc}) = 50.5 \times \rho^{0.9}$. The agreement is a trifle closer but there is no great difference. The result of the comparison of Stodola's and Lewicki's wheels is to show that as nearly as we can tell, equation (9) represents the facts and that dry steam is entirely comparable with air when the proper physical constants are used.

We may now consider Lewicki's five observations in saturated steam, the results of which are shown in Table 3.

TABLE 3

Lewicki's Observations in Saturated Steam; n = 20 000 r. p. m.

Pressure p [lb./in.^{2}]	**Density** ρ [lb./ft.^{3}]	**Power** P [U. S. hp.]	$\frac{P}{\rho}$	$\frac{P}{\rho^{0.9}}$
14.7	0.03732	3.22	86.2	62.0
10.50	0.02727	2.69	98.3	68.9
8.56	0.02253	2.05	91.1	63.7
6.44	0.01726	1.66	96.0	64.0
5.69	0.01538	1.49	96.8	63.7
Mean	0.02395		93.7	64.5
Mean residuals			±4.3%	±2.8%

As for superheated steam, we can represent the results approximately by $P \propto \rho$ or $P \propto \rho^{0.9}$, the second being in this case distinctly the better, as is shown by the fact that the mean residual is only 2.8 per cent as compared with 4.3 per cent.

Not knowing how the viscosity varies with temperature when the steam is kept saturated, we ignore the last factor of equation (14) which is certainly nearly unity, and we then have $P(\text{calc}) = 49.7\rho^{0.9}$ as compared with $P(\text{obs}) = 64.5\rho^{0.9}$. The observed value is thus 1.30 times the calculated. Making the computation by the mean density we have $P = 93.7\rho$, $\rho = 0.02395$ $P(\text{obs}) = 2.23$ hp while equation (14) gives us $P(\text{calc}) = 1.73$, the ratio being now 1.29 in place of 1.30.

The cause of the discrepancy of 30 per cent is clear. To obtain dry saturated steam is a difficult matter, requiring elaborate precautions, though this was not so well known at the date of Lewicki's experiments. The increase of 30 per cent in the resistance in passing from air or dry steam to saturated steam, was due to the wetness of the steam. Not knowing how wet the steam may have been, we have, perforce, used the density of the steam alone and not the mean density of the mixture. The mean density would have been larger and so would, if used in the computations, have reduced the discrepancy between the observed and calculated values. But it is most unlikely that the steam was so wet that the whole 30 per cent could be accounted for in this way, even supposing that the water remained completely suspended. And under such conditions only a very small amount of water remains in suspension as fog; most of it is deposited and that is undoubtedly what happened here. Just how wet the steam was and why the deposition of water on the wheel should have increased the resistance 30 per cent it is of course impossible to say. But it is clear that the steam did not act like an *homogeneous* medium, so that equations developed for homogeneous media, which, as we have seen, describe the facts satisfactorily for both air and dry steam, are not strictly applicable. All we can say at present is that the resistance to the rotation of a wheel in steam increases considerably if the steam changes from dry to wet; but how the amount of the increase depends on the wetness or other circumstances can only be decided by further experiments.

It remains to examine Holzwarth's results for wheels which had the same ratio of blade height to disk diameter and so had at least this one element of geometrical similarity. We have the figures given in Table 4, for $\frac{l}{D} = 0.05$.

TABLE 4

Holzwarth's Results on Wheels with the same Blade Length Ratio

Disk diameter D (ins.)	Blade length l (ins.)	Speed exponent β	$\frac{10^{16}K}{n^3D^5}$
20	1.0	3.6	2.5
30	1.5	3.0	3.5
40	2.0	2.9	2.5
50	2.5	3.1	2.3

The values of β, taken from the straight lines drawn on the plot of log K against log n vary considerably and are rather uncertain so that the round values $\beta = 3$ and $\gamma = 5$ have been adopted. The values in the last column were got by averaging over all the points which lay distinctly above any indication of a rapid change in the exponent of n, omitting a few doubtful readings. If these wheels were, together with their casings, all geometrically similar, and if we had $\delta = 0$, the values of $\frac{10^{16}K}{n^3D^5}$ should all be the same; it is seen that they are nearly so. The high value for the 30-inch wheel is consistent with other readings which make it appear that the 30-inch disks were much rougher than those of the other diameters.

We have also the following figures for $\frac{l}{D} = 0.025$

TABLE 5

D	l	β	$\frac{10^{16}K}{n^3D^5}$
20	0.5	3.6	1.31
40	1.0	2.5	1.29

If the readings of K from the published curves really represent the facts as Holzwarth observed them, the great difference in the two values of β proves that these two wheels were far from geometrically similar. The agreement of the values in the last column is therefore little better than accidental, though it shows that the facts may be represented, at least roughly, by the equation $P = N\rho n^3D^5$.

5. *The Effect of the Density of the Medium.*—All writers on the subject appear to agree that when a given wheel runs at a given speed, the power dissipated is directly proportional to the density of the medium. Holzwarth says that this relation holds for steam "within limits accurate enough for practical purposes," and Lasche, in an equation quoted by Stodola,[1] sets $P \propto \rho n^3$. Stodola experimented on a multi-disk impulse turbine driven in stagnant steam of densities of 0.1 to 1.7 kgm/m^3, which correspond, if the steam was dry saturated, to pressures of 2.5 to 45 lb/in^2 absolute. His observations as plotted on a small scale diagram indicate the existence of a linear relation between P and ρ, and he sets $P \propto \rho$ and uses this relation without further question. Lewicki's observations as given in Tables 2 and 3 also indicate that the resistance is approximately proportional to the density. We may therefore say that within the range

and the accuracy of the published experimental data on this point, the windage of turbine wheels in a given medium is proportional to the density of the medium, but the evidence is not at all sufficient to show how nearly exact the relation is. We can, in fact, only regard this evidence as roughly conformatory of that presented in section 3, which shows that when the medium is homogeneous the exponent of ρ in equation (7) can not differ much from unity.

6. *Remarks on the Comparison of Dissimilar Wheels.*—The considerations already set forth having shown that an equation of the form (7) describes the behavior of wheels of any one shape, it remains for us to find out if possible how the coefficient N depends on the shape of the wheel and its casing.

Since N depends on shape and not on absolute size, any correct expression for N must contain as variables only ratios of lengths. An equation for P which can not be reduced to the form (3), or practically to the form (7), with the N's satisfying the above condition, is not a rational equation and can not have any general validity, even approximate, though it may be satisfactory as an empirical working formula over limited ranges of the variables.

In attacking the problem of finding a satisfactory expression for N we are met at the outset by the obvious fact that the shape of a turbine wheel and its casing, even if confined to general conformity with commercial practice, may vary in a great many ways. Thus N must be regarded as a function of a large number of variables which are, at least within certain limits, all independent. But while a complete solution of the problem of predicting the value of N from geometrical measurements is thus out of the question, we may nevertheless make some progress if it is found that in practice one or a very few variables are of so much importance that the effects of changing the others are small or negligible.

It is evident, both a priori and from experiment, that two very important geometrical elements to be considered are the blade length and the closeness with which the casing surrounds the blades, both measured in terms of the disk diameter. Other important elements are the roughness of the disk; the width, pitch, and angles of the blades; the number of rows of blades, and whether they are shrouded or not. Of these most evidently important data, the blade length ratio, $\frac{l}{D}$, and the number of rows of blades are often the only ones given in published accounts of experiments, the others either not being given at all or having been varied so unsystematically that they can not be used. To start with, we shall of necessity confine our attention to wheels with one row of blades, together with their limiting form, bladeless disks. As regards pitch, width, and angles of the blades, we can only say that in practice different single-row steam-turbine wheels are usually somewhere near similar in respect to these points, as they are also, though perhaps less nearly, in respect to roughness and profile of the disk.

Stodola's experiments[1] showed that the amount of clearance between wheel and casing has a large influence on the windage resistance, and he made a few measurements relating to this piont. But since his results are not numerous and we have no other satisfactory data on the effect of altering the casing which incloses a given wheel, we are reduced to the expedient of eliminating the effect of the casing by removing it altogether; in other words, we must, at least in starting, use only data obtained from wheels running in the open without any casing. We may then hope to get an approximate expression for N in terms of the blade-length ratio, the hope being founded on the expectation that this will prove to be much more important in specifying the shape of the wheel itself than all the other variable elements combined, so long as these others remain within the limits which obtain in practice.

We then have available for study, Odell's results on disks and Stodola's results on one disk and five wheels. Tentatively, we shall also use Holzwarth's results on inclosed wheels in steam, the assumption being that the casings were similar. Since the nature of these data does not warrant the use of any refinements in analyzing them, we shall accept the equation

$$P = N\rho n^3 D^5 \qquad (15)$$

as a sufficiently approximate description of the facts for wheels of any given shape.

7. *Expressions for N in terms of Roughness and Blade Length.*—If we assume that the differences of resistance of different single-row wheels of the same disk diameter, when driven at the same speed in the same medium, are expressible in terms of the roughness of the disk and the blade length l, the coefficient N must have the form

$$N = A + f\left(\frac{l}{D}\right) \tag{16}$$

in which f is some function which vanishes with its argument, and A is the constant limiting value of N when the blades are shortened indefinitely. For simple flat wheels the "disk coefficient" A will depend mainly on the superficial roughness of the metal of the disk; but it will also, in general, depend on the profile of the wheel and the nature of the shrouding over the ends of the blades. For brevity we may include all these factors in the single term "roughness" since we have no data which would enable us to separate them.

If, further, we admit that equation (7) is correct in having only a single term in the second member, it follows that any general equation for P which contains no other elements of shape than roughness and blade length must necessarily have the form

$$P = \rho^{1-\delta} n^{3-\delta} D^{5-2\delta} \mu^{\delta} \left[A + f\left(\frac{l}{D}\right)\right] \tag{17}$$

or approximately

$$P = \rho n^3 D^5 \left[A + f\left(\frac{l}{D}\right)\right] \tag{18}$$

The three equations which the writer has seen given for computing the power dissipated in windage, do not satisfy this requirement and so are not general, i. e., they can not safely be used for extrapolation to values of the variables outside the limits of the experiments from which the equations were deduced. These three equations are the following:

Lasche is quoted by Stodola[1] as having deduced, from experiments on wheels with 1, 2, 3, and 4 rows of blades, equations which may, for comparison with (18) be written in the form

$$P = \rho n^3 D^5 \left[B\left(\frac{l}{D}\right) D^{-3}\right] \tag{19}$$

This equation does not profess to be valid except within rather narrow limits, hence there is no occasion for criticising the fact that it leads to an absurdity for bladeless disks or that it violates the dimensional requirements.

Jude,[9] after an examination of the experimental results of Odell, Lewicki, Stodola, and Holzwarth, gives an equation which may be written

$$P=\rho n^3 D^5\left[A+B\left(\frac{l}{D}\right)^{\frac{1}{4}}D^{-2}n^{-\frac{1}{4}}\right] \tag{20}$$

The second or blade term of this equation violates the dimensional conditions completely.

Stodola [1] gives an equation which may be written

$$P=\rho n^3 D^5\left[A+B\left(\frac{l}{D}\right)^{\frac{3}{2}}D^{\frac{1}{2}}\right] \tag{21}$$

This, too, violates the dimensional requirements but to a less extent than equation (20); it could therefore be used over a wider range of diameters before involving excessive errors. Equation (20) can apply only over a limited range of speed as well as of diameter, while equation (21) involves time correctly to the same degree of approximation as equation (15).

It has seemed to the writer worth while to attempt to represent the same data as were used by Stodola and Jude, or such of them as it appeared might legitimately be used, by an equation which should be free from the defects just noticed. The very simple form

$$P=\rho n^3 D^5\left[A+B\left(\frac{l}{D}\right)^{x}\right] \tag{22}$$

was therefore tested, to see if it was possible to find satisfactory values of the constants A, B, and x. The disk coefficient, A, must evidently depend on the roughness of the disk and we can not expect all disks to give the same value. The "blade coefficient," B, should doubtless involve the width, pitch, angles, profile, and form of shrouding of the blades, but it will, tentatively, be treated as a constant, as will the exponent x. The question is whether such an equation can be made to describe the observed facts with reasonable accuracy and completeness.

8. *The Form of the Coefficient N for Stodola's Unenclosed Wheels.*—We may first examine Stodola's data on his five wheels running in the open air. He gives his observed value of the power absorbed by each wheel, only for one speed, namely the highest used with that wheel. The data which concern us here are collected in Table 6.

TABLE 6

Stodola's Observations on Unenclosed Wheels in Air

I	II	III	IV	V	VI	VII	VIII
	$\frac{l}{D}$	Disk diameter D (ins)	Maximum speed n (r. p. m.)	Power absorbed P (hp.)	$10^{16}N$	P (calc)	P (obs) $-P$ (calc) in per cent
D	0.0311	34.84	1600	2.306	1.569	2.315	− 0.4
C	0.0364	26.50	2200	1.778	1.786	1.736	+ 2.4
A	0.0396	19.88	2200	0.536	2.319	0.446	+18.
E	0.0476	45.47	980	2.895	2.264	3.000	− 3.5
B	0.1190	19.84	2100	1.850	9.306	1.833	+ 0.9

N is defined by $P=N\rho n^3D^5$ and the density of the air is assumed to have been $\rho=0.0699\ lb/ft^3$

$$P\ (\text{calc})=10^{-16}\rho n^3D^5\left[1+593\left(\frac{l}{D}\right)^2\right]$$

If the observed values of P. are expressible by equation (22), i. e., by setting $N=A+B\left(\frac{l}{D}\right)^x$, we have

$$\log\ (N-A)=\log\ B+x\ \log\ \frac{l}{D} \tag{23}$$

and the values of A, B, and x may be found by trial. We assume a value of A, and plot $\log\ (N-A)$ against $\log\ \frac{l}{D}$. If we can find a value of A such that the points all lie on a straight line within the observational errors, equation (22) is satisfied, the slope of the line is the value of x, and the position of the line gives the value of B.

By this method it was found that the observations on four of the five wheels are satisfactorily represented by writing equation (22) in the particular form

$$P=10^{-16}\rho n^3D^5\left[1+593\left(\frac{l}{D}\right)^2\right] \tag{24}$$

and that no other values of A, B, and x are sensibly better. Values computed by equation (24) are given in column VII of Table 6 and the agreement of the results with the observed values in column V is shown by column VIII to be good except for wheel A. The value for this wheel can evidently not be brought into accord with those observed for the others by any simple expression for N as a function of $\frac{l}{D}$. It is possible that the discrepancy may be due to an experimental error, but this seems very unlikely. Unless it is merely a typographical error, it probably arises from some geometrical peculiarity of this wheel which is not evident from the description given. The writer has assumed that the blades of all the wheels were shrouded, because that is the usual construction; but if the blades of wheel A were open-ended, the relatively greater windage would be easily understood.

However, there is no advantage to be gained from splitting hairs in analysing so small a number of data by means of confessedly only roughly approximate assumptions, and we may be content to say that equation (24) represents the results of Stodola's experiments on single-row wheels of ordinary forms running in the open air, quite as well as could be demanded of any equation deduced from so inadequate data.

9. *Deduction of an Expression for N from Holzwarth's Data.*—Holzwarth's results and the manner in which they were treated for finding the relation of P to n, have been described in section 3. The values found for $\beta = 3 - \delta$ are given in Table 7 as they were read from the straight lines drawn on the plot of log K against log n and they are uncertain by from 0.1 to 0.2, because the lines were drawn merely by inspection.

TABLE 7

Values of K from Holzwarth's Diagrams

Blade length (inches)	$D=20$ inches	$D=30$ inches	$D=40$ inches	$D=50$ inches
0.5	3.61	3.39	2.51	3.24
1.0	3.62	3.00	2.51	3.30
1.5	2.28	3.00	2.58	2.58
2.0	2.83	2.98	2.90	2.89
2.5	2.69	3.39	3.09	3.14

From the great variations in β it appears either that the values of Holzwarth's coefficient K read from his diagrams are erroneous or that the wheels, even for the same blade-length ratio, were far from geometrically similar. It would be a waste of time to attempt to reconcile all the readings of K with an equation of the form (22) in which $\beta = 3$, and I have therefore arbitrarily selected the eight series which gave values of β (*italicized* in Table 7) between 2.8 and 3.2, i. e. values which we can not be sure are different from 3.0, and I shall confine my analysis to these series.

For each of the selected eight series, the mean value of $\frac{10^{16}K}{n^3D^5}$ was found by averaging over all the values of K for the higher speeds, omitting a few points where the readings from the diagrams were obviously liable to exceptionally large errors. We thus get eight separate values.

In the units we have been using we have, approximately,

$$P = 0.54\,\rho\,K \tag{25}$$

Since Holzwarth's diagrams are drawn for a constant value of the density we may treat K as we have previously treated P, which is proportional to it when ρ is constant. If we proceed in this way, we find that by selecting an appropriate disk coefficient A' for each diameter and plotting $\log\left(\frac{10^{16}K}{n^3D^6} - A'\right)$ against $\log\frac{l}{D}$, seven of the eight points may be made to fall very close to a single straight line of which the slope is 2. The exception is the one rather doubtful point for the 20-inch diameter. We thus find that those of Holzwarth's results which are comparable with Stodola's in giving $\beta = 3$, approximately, may be represented by an equation very like (24) which describes Stodola's results. The exponent of $\left(\frac{l}{D}\right)$ is the same and the disk and blade coefficients are not very different, though somewhat smaller for Holzwarth's wheels, in accordance with the fact that the wheels were inclosed instead of run in the open.

If we write

$$P = \rho n^3 D^5\left[A + B\left(\frac{l}{D}\right)^2\right] \tag{26}$$

we have the values of A and B given in Table 8.

TABLE 8

Values of the Coefficients of Equation (26)

	Disk diameter D (inches)	Disk coefficient $A\times10^{16}$	Blade coefficient $B\times10^{16}$
Stodola's observations on wheels B, C, D, E, in open air	19.8–45.5	1.0	593
Holzwarth's observations. Wheels inclosed in steam	20	(0.54)	(243)
	30	0.86	414
	40	0.32	414
	50	0.22	414
Stodola's bladeless disk run in open air	21.1	0.63	
Odell's disk D in open air	47.1	0.5	
Jude; from observations by Lewicki, Odell, Stodola, and Holzwarth, for wheels run in open air		0.44	

The difference between the coefficients deduced from Stodola's and from Holzwarth's observations would probably have been greater if Holzwarth's values had all been obtained from experiments in air. His results were obtained "from occasional experiments carried on for some years—partly in air, partly in steam of different density." Since he says nothing to the contrary, the steam was doubtless saturated and probably by no means dry, so that we may infer from Lewicki's observations, described in section 4, that the value of N or of the coefficients A and B would have been smaller if the experiments had all been made in air or perfectly dry steam.

On account of the varying density in Holzwarth's experiments, some sort of reduction to a standard density must have been made in order to get the values of K for drawing the diagrams. Holzwarth sets $P\propto\rho$ and we must assume that he used this relation in the reduction. But if in equation (7) the value of β is very different from 3, the exponent of ρ must differ by the same amount from unity and a reduction of this sort is not permissible. Although no detailed criticism is possible, it is evident that we have here an additional ground for omitting from consideration those series of Holzwarth's results which do not conform approximately to the equation $P=const\times n^3$.

The degree of approximation to which equation (26) with the coefficients given in Table 8 reproduces the readings from Holzwarth's diagrams, may be seen from Table 9 in which are given the values *K*(obs) read from the diagrams, and the values *K*(calc) computed from equations equivalent to (26) with the coefficients in Table 8. The readings may be in error by one unit at the low values and several units at the higher.

TABLE 9

Comparison of Observed and Computed Values of Holzwarth's Coefficient *K*

Speed in r. p. m. n=			1000	1250	1500	1750	2000	2500	3000	3500
D (in.)	*l* (in.)									
20	2.0	obs	5	6	8.5	10	14.5	24.5	45.5	(120)
		calc	....	....	5.9	9.4	14.1	27.5	47.5	75.5
30	1.0	obs	10.5	13.5	20	31.5	45	94	160	293
		calc	6	11.6	20.1	31.9	47.7	93.1	161	256
	1.5	obs	12.5	19	28.5	44	62.5	131	238	......
		calc	8.5	16.7	28.8	45.8	68.3	133	231	......
	2.0	obs	13	20	40	70	109.5	205	344	......
		calc	12.2	23.8	41	65.2	97.3	190	328	......
40	2.0	obs	26	46	85	150	224	375	527	......
		calc	25.7	50.3	86.9	138	206	402	695	......
	2.5	obs	34	63	123	211	334	560	....	......
		calc	36.8	71.8	124	197	294	574	....	......
50	2.0	obs	50	86.5	161	288	....	....	....	......
		calc	50.8	99.2	172	272	....	....	....	......
	2.5	obs	65	118	236	446	....	....	....	......
		calc	72.3	141	244	388	....	....	....	......

For the smaller wheels the observed resistance at the lower speeds is considerably larger than the calculated, and the law of resistance is evidently not the same as at the high speeds. At 750 r. p. m. the observed *K* is larger than the calculated in every instance. But if we omit the low speeds, where agreement is not to be expected, and the highest speeds, where slight errors in the drawing of the diagrams cause large errors in the values of *K* read from them, the agreement of observed and calculated values is fair—certainly as good as would be demanded of any formula by one who has studied the diagrams.

10. Further Values of the Disk Coefficient.—We have now exhausted the few published data which are available for investigating the dependence of the coefficient N of equations (7), (8), (9), etc., on the blade-length ratio, and there remain for consideration only experiments on bladeless disks which will give values of the disk coefficient for comparison with the values obtained from experiments on wheels with blades.

Stodola's boiler-plate disk of 21.1-inch diameter absorbed 0.147 hp when running 2000 r. p. m. in air of density $\rho = 0.07$ lb. per cu. ft^3. From these values we find $A = 0.63 \times 10^{-16}$. The only remaining experiments on a rigid disk, which gave $\beta = 3$ nearly, are those of Odell on his largest disk. From data already given in section 4 we find for this disk $A = 0.5 \times 10^{-16}$ approximately. Both these values are included in Table 8. The difference between the values of A deduced from Stodola's observations on wheels and on the disk need not cause any surprise, for we do not know anything about the relative roughness in the two cases. The shrouding over the blades and the difference of profile between wheels and disk may account for the difference, which appears to be genuine.

One more value of A is included in Table 8, namely, $A = 0.44 \times 10^{-16}$, deduced by Jude from a general examination of all the experiments already mentioned in this paper. It is applicable according to its author to flattish disks in open air.

11. The Influence of Axial Clearance.—For information on this point we have only Stodola's comparative runs of three of his wheels in the open air and in casings. The results are given in Table 10, some of the data being repeated from Table 6.

TABLE 10

Stodola's Experiments on Varying Clearance

I	II $\frac{l}{D}$	III D inch	IV Axial clearance $\div D$	V $10^{16}N$	VI Ratio
			∞	2.32	
A	0.0396	19.88	0.0079	1.28	0.55
				2.26	
E	0.0476	45.47	0.0056	0.57	0.25
			∞	9.31	
B	0.1190	19.84	0.0079	3.53	0.38

In column V of the table are given the values of N in the equation $P = N\rho n^3D^5$ for the axial clearances given in column IV, the clearance ∞ meaning that the wheel was run in the open air. In column VI there is given for each wheel the ratio in which the dissipation was reduced by the presence of the casing.

It appears from this table that the effect of a close casing is much greater on the blades than on the disk. By comparing wheels A and B we find that the presence of a casing, which left at the blade edges an axial clearance of about 0.008 times the disk diameter, reduced the resistance considerably more in the case of B, which had blades three times as long as those of A, the ratio of reduction being 0.38 for the long blades as against 0.55 for the short ones. If we compare wheels A and E, which did not differ very widely as to blade-length ratio, we find that reducing the clearance from 0.0079 D to 0.0056 D, i. e., to two-thirds, decreased the resistance, expressed as a fraction of the open-air resistance, by about one-half, or from 0.55 to 0.25. We have also already found in section 4, when comparing wheel B with Lewicki's wheel of about the same blade-length ratio, that increasing the axial clearance by about one-half, or from 0.008 D to 0.012 D, increased the resistance some 35 per cent.

These few isolated data are evidently not a sufficient ground for any general quantitative statement about the effect of clearance on windage, but they may be valuable as a basis for guesswork in cases which happen to be nearly similar to the ones mentioned.

In this connection we may also note the results obtained by Stodola[1] in comparing wheels run in the normal or forward direction with the same wheels run backward. In open air the resistance backward was in one example as much as 5.4 times the resistance forward, though in other examples the ratio was not so large. But inclosing the blades reduced the difference very much, and the longer the blades and the greater the part of the resistance due to the blades the greater is this effect of the casing, so that with very small clearances the resistance when the wheel is run backward is very little greater than when it is run forward. With wheel B for which $\frac{l}{D} = 0.119$, when the axial clearance was 0.008 D, the resistance backward was only 13 per cent more than the resistance forward.

12. *Remarks on Further Experimental Results.*—In the foregoing discussion the symbol P has everywhere denoted the power required to drive a wheel against the resistance of the otherwise stagnant medium surrounding it, and the experiments noted have referred to this state of affairs. But the conditions of ordinary practice are different, and it remains a question whether, in designing a steam turbine, a windage correction based on even completely satisfactory data of the kind considered could be considered reliable. The only answer that can be made to this question is that we do not know; and the best, because the only, thing we can do at present is to compute windage corrections for designing purposes as if the turbine were to be driven independently from without, acting merely as a brake, a condition which occurs only in the case of marine turbines with reversing stages or with cruising stages which are by-passed at full power.

Another pertinent question is: How much ought the computed windage loss to be reduced when a part or all of the blades are working in the ordinary manner, with steam from the nozzles passing through them? The experiments of Lasche, quoted by Stodola,[1] and of Jasinsky [10] are not sufficiently comprehensive to tell us more than that the windage decreases as the admission arc increases and fewer blades are idle. With rectangular nozzles and a continuous steam belt, it will probably be not far wrong to multiply the blade term of the computed resistance by the fraction of the whole circumference which is not occupied by open nozzles, i. e. by the fraction of the whole number of blades which is idle at each instant.

The experiments we have considered having referred only to disks or single-row wheels, one further question remains: How does the windage, i. e. the value of N in our equations, depend on the number of rows of blades? Here again we have only the most meager information. Experiments by Lasche, quoted by Stodola,[1] gave for wheels with from 1 to 4 rows but otherwise, presumably, similar, resistances which stood in the following relation:

Number of rows of blades	1	2	3	4
Relative resistance	1	1.2	1.6	2.4

But the experiments were on wheels which were not closely encased so that they do not give us much practical assistance. The increase of resistance with number of rows of blades would probably be very much less rapid if the wheels were run in casings with fine clearances.

13. *Dynamically Similar Wheels.*—The one fact which emerges clearly from the foregoing discussion is that the task of providing data for the development of a satisfactory general formula for computing the windage losses of high-speed steam turbines, has hardly been begun. Suggestions as to future lines of experiment are therefore in place here.

Up to peripheral speeds of at least one-half the speed of sound, or about 700 feet per second for steam, we are justified in treating the medium as incompressible and the resistance phenomena may be described by an equation of the general form (4). If we introduce the "kinematic viscosity" $\nu = \frac{\mu}{\rho}$, the equation may be written

$$P = \rho n^3 D^5 \varphi\left(\frac{\nu}{nD^2}\right) \tag{27}$$

φ being a function of which the form, though unknown, is fixed by the shape of the wheel and casing.

Let us compare two geometrically similar wheels of diameters D and D_0 running in media of densities ρ and ρ_0 and kinematic viscosities ν and ν_0 at speeds of rotation which stand in the ratio

$$\frac{n}{n_0} = \frac{\nu}{\nu_0}\left(\frac{D_0}{D}\right)^2 \tag{28}$$

Speeds thus related are "corresponding speeds."

At corresponding speeds

$$\frac{\nu}{nD^2} = \frac{\nu_0}{n_0 D_0^2}$$

and since the *form* of φ depends only on the shape, which is the same for the two wheels, we have

$$\varphi\left(\frac{\nu}{nD^2}\right) = \varphi\left(\frac{\nu_0}{n_0 D_0^2}\right)$$

no matter what the shape of the wheels and the form of the function φ may be. The ratio of the dissipation by the two wheels at corresponding speeds is therefore, by equation (27)

$$\frac{P}{P_0}=\frac{\rho n^3 D^5}{\rho_0 n_0^3 D_0^5}$$

or by equation (28) which defines corresponding speeds,

$$\frac{P}{P_0}=\frac{\rho}{\rho_0}\left(\frac{\nu}{\nu_0}\right)^3\frac{D_0}{D} \qquad (29)$$

Any two geometrically similar wheels running at corresponding speeds constitute a pair of "dynamically similar" systems, and the power dissipated by either may be determined from an experiment on the other by means of equation (29), if the diameters of the wheels are measured and the densities and kinematic viscosities of the media are known.

If the experiments are all made in the same medium so that $\rho=\rho_0$ and $\nu=\nu_0$, corresponding speeds are inversely as the squares of the diameters and the powers dissipated at corresponding speeds are inversely as the diameters.

If T and T_0 are the torques required to drive the wheels at corresponding speeds, since $P \propto nT$ we have by (28) and (29)

$$\frac{T}{T_0}=\frac{\rho}{\rho_0}\left(\frac{\nu}{\nu_0}\right)^2\frac{D}{D_0} \qquad (30)$$

At corresponding speeds in a given medium the torque is directly as the diameter.

The shearing stress in the metal of the shaft, so long as the shaft is not sensibly distorted, is proportional to the torque divided by the cube of the shaft diameter, or with similar wheels to $\frac{T}{D^3}$. Hence the ratio of the shearing stresses, S and S_0, in the shafts of two dynamically similar wheels is

$$\frac{S}{S_0}=\frac{\rho}{\rho_0}\left(\frac{\nu}{\nu_0}\right)^2\left(\frac{D_0}{D}\right)^2 \qquad (31)$$

At corresponding speeds in a given medium the shearing stresses are inversely as the squares of the diameters.

The centrifugal stresses C and C_0 in the metal of the two wheels, if they are of the same density, will stand approximately in the ratio.

$$\frac{C}{C_0}=\left(\frac{\nu}{\nu_0}\right)^2\left(\frac{D_0}{D}\right)^2 \tag{32}$$

At corresponding speeds in a given medium, the centrifugal stresses are inversely proportional to the squares of the diameters if the wheels are of the same density.

14. The Use of Model Wheels in Studying Windage.—To avoid the difficulties of working with large wheels, it may be desirable to utilize the results of model experiments as is done in determining ship resistance.

If we limit ourselves to the use of a single medium, the practicable range of scale reduction is not great, unless the full-sized original runs very slowly, and this case is not interesting because we know that at low speeds the windage losses are too insignificant to demand much attention. For dynamical similarity in a given medium, a quarter-scale model must, by equation (28) run at 16 times as many revolutions per minute as the full-sized original; and by equation (32), the centrifugal stresses in the wheel will then be 16 times as great in the model as in the original; an increase which would usually not be permissible. Furthermore, the peripheral speed of the model will be 4 times that of the original and may approach the acoustic speed so closely as to invalidate our fundamental assumption that the medium behaves sensibly as if it were incompressible. There is evidently not much information to be got from small scale models unless they can be run in a medium of much less kinematic viscosity than steam, so that the speed of the model may be reduced, in accordance with equation (28).

Water is such a medium. Using values from Landolt and Börnstein's tables, and comparing water with air which is known to act like dry steam, we have at 20° C and 1 atmosphere pressure.

Air	Water
$\rho=0.001205$ $\mu=0.0001898$ $\nu=0.1575$	$\rho=0.9982$ $\mu=0.01012$ $\nu=0.01014$

Let it be desired to find the power dissipated by a wheel of diameter D_0 running n_0 revolutions per minute in air, by means of experiments on a model of diameter $D = \frac{D_0}{r}$ running in water, the temperature being 20° C in each case and the air being at normal pressure. We then have to substitute in equations (6) to (10)

$$\frac{\rho}{\rho_0} = 828 \qquad \frac{\nu}{\nu_0} = 0.0644$$

the uncertainty of $\frac{\nu}{\nu_0}$ being about ± 3 per cent.

For any given scale ratio r, the ratio of corresponding speeds, n for the model and n_0 for the original will be, by equation (28),

$$\frac{n}{n_0} = 0.0644 r^2 \pm 3 \text{ per cent} \tag{33}$$

The ratio of the powers dissipated at corresponding speeds will be, by equation (29),

$$\frac{P}{P_0} = 0.222\ r \pm 6 \text{ per cent} \tag{34}$$

from which P_0 can be found if P has been measured in an experiment on the model.

We must next consider whether the stresses in the wheel and shaft of the model will rise too high when we make a convenient reduction of diameter. Taking first the centrifugal stresses in the wheel, we have by substitution in equation (32)

$$\frac{C}{C_0} = 0.00415\ r^2 \tag{35}$$

Setting $C = C_0$ and solving for r, we find that the stress of any point in the model will not exceed that at the corresponding point in the original until $r > 15.7$. As a 10 to 1 reduction will usually be ample, there will be no difficulty regarding the bursting strength of the model if it is made of the same material as the full-sized wheel.

For the ratio of the shearing stresses in the shaft, equation (31) gives us

$$\frac{S}{S_0} = 3.43\, r^3 \tag{36}$$

A scale reduction $r = 10$ would thus give us 343 times as great a stress in the shaft of the model as in the original shaft. This, at first sight, looks quite impracticable. But in fact turbine shafts are generally made much stronger, for the sake of stiffness, than is required by torsional strength; and, furthermore, the torque due to windage when the wheel is driven light is only a few per cent of the torque of the wheel running at full load. Hence the ratio 343 would probably not always be excessive. However, doubling the diameter of the shaft of the model would have hardly any effect on its windage resistance, and by such a small sacrifice of exact geometrical similarity the use of a model in water might always be made practicable, so far as the strength of the shaft is concerned.

To make the matter more concrete we may carry out the computations for a few typical cases of wheels run in air in comparison with models of 12 inches diameter run in water. We have the values given in Table 11.

TABLE 11

Full-sized diameter D_0 (inches)	**Wheel speed** n_0 (r. p. m.)	**Diameter ratio for 12-inch model** $r = \frac{D_0}{D}$	**Speed of model** n (r. p. m.)	**Power ratio** $\frac{P}{P_0}$	**Stress ratio in shafts** $\frac{S}{S_0}$
36	3600	3	2090	0.67	31
60	1800	5	2900	1.11	86
84	900	7	2840	1.55	168
120	450	10	2900	2.22	343

It therefore appears that the investigation of such cases as are commonly met with, by means of 12-inch models run in water, would be quite practicable so far as the points already treated are concerned, and only one further point remains to be considered. This is the question of cavitation.

If cavitation occurs in the water the similarity of the model and the original will cease to exist, and equation (29) will not give correct results. To avoid cavitation, the water surrounding the model must be under pressure and the casing must be constructed accordingly. At atmospheric pressure and high speeds cavitation will certainly occur. If the pressure on the water is increased the cavitation will decrease and the torque at a fixed speed will change until the pressure has been increased so much that cavitation has been eliminated. By observing the variation of torque or power with the pressure at any given speed we have thus a means for finding what pressure is needed in order to eliminate cavitation and make sure that the model in water is comparable with its original in air or steam. It remains to be seen whether the pressures required would be impracticably high, but it appears that the method of model experiments is worth trying.

15. *Summary.*—I. The power P required to drive a turbine wheel of diameter D at n revolutions per unit time against the resistance of a homogeneous medium of density ρ and viscosity μ, when the peripheral speed does not exceed one-half that of sound, may be represented by an equation of the general form

$$P = \rho n^3 D^5 \varphi\left(\frac{\mu}{\rho n D^2}\right) \tag{I}$$

in which the form of the unknown function φ depends solely on the shape of the wheel and its casing.

II. Throughout the practical range of the experimental data, equation (I) has the simpler form

$$P = N \rho^{1-\delta} n^{3-\delta} D^{5-2\delta} \mu^{\delta} \tag{II}$$

the abstract numerical constant N having a value which is determined solely by the shape of the wheel and casing. All the reliable data which we have agree with equation (II) or with direct deductions from it.

III. At low speeds the value of δ is nearly unity and the resistance is directly proportional to the viscosity of the medium. At the speeds at which stationary turbines are usually run, δ is a small quantity and we have approximately

$$P = N\rho n^3 D^5 \qquad \text{(III)}$$

A closer approximation is obtained by setting $\delta = 0.1$ whence

$$P = N\rho^{0.9} n^{2.9} D^{4.8} \mu^{0.1}$$

IV. For wheels of ordinary shapes, running either in the open or in casings with fairly large clearances, the "shape coefficient" N may be expressed approximately by the equation

$$N = A + B\left(\frac{l}{D}\right)^2 \qquad \text{(IV)}$$

in which l/D is the ratio of the blade length to the disk diameter. The disk coefficient A increases with roughness of the disk; the blade coefficient B decreases when the clearance round the blades is decreased, but no more definite statements are warranted.

V. (*a*) For designing purposes we may first compute the windage loss by the following equation deduced from Stodola's results:

$$P = 10^{-16} \rho n^3 D^5 \left[1 + 590\left(\frac{l}{D}\right)^2\right] \qquad \text{(V)}$$

In this equation

P = the horsepower dissipated
ρ = the density of the medium, in pounds per cubic foot
n = the speed, in revolutions per minute
D = the diameter, in inches, at the root of the blades
l = the length of the blades, in inches

The equation is applicable to wheels of ordinary shapes with one row of shrouded blades, running in the open or in casings which leave large clearances, in a homogeneous medium such as air or dry steam.

(*b*) Reducing the clearances, especially round the blades, reduces the windage. In some cases the amount of this reduction may be estimated from Table 10 but no general quantitative statement is possible. The reduction affects mainly the blade term.

(*c*) Open-ended blades have more resistance than shrouded blades, to which equation (V) refers, but there are no data to show how much. When the radial clearance over the blade tips is small, the presence or absence of shrouding will have little effect.

(*d*) A wheel run backward experiences a greater resistance than the same wheel run forward, i. e., in the normal direction. When running in the open the difference may be considerable, but if the clearances round the blades are small, the resistance backward is not much greater than the resistance forward.

(*e*) Each additional row of blades increases the resistance. When run in the open, a four-row wheel may have two and one-half times the resistance of a one-row wheel, but there are no adequate data published. With short blades and fine clearances the effect of increasing the number of rows will be much less than that indicated.

(*f*) A wheel run in wet steam experiences more resistance than in dry steam or air of the same density. In Lewicki's experiments the increase was 30 per cent; we have no other information on this point.

(*g*) Equation (V) gives the power absorbed when the wheel is driven from without. If the wheel is working in the usual manner we may reduce the blade term in the ratio of the number of idle blades to the whole number.

(*h*) The values given by equation (V) may be too large, especially for smooth wheels with short blades; for the disk coefficient used, viz.: $A = 10^{-16}$, is larger than the values deduced from other experiments.

VI. The necessary indefiniteness of many of the statements made under V is due to lack of experimental data. No formula based only on our present knowledge can be trusted to give accurate results, and no formula which has not the general form (II) should be used for extrapolation beyond the limits of the experiments from which it was deduced. Equation (V), if used as indicated, probably gives safe maximum values.

VII. The method of model experiments is applicable to the study of the windage losses of steam turbines and might prove very useful by decreasing some of the difficulties encountered in making systematic experiments on a large number of full-sized wheels.

WASHINGTON, July 25, 1913.

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LATENT HEAT OF FUSION OF ICE

By H. C. Dickinson, D. R. Harper 3d, and N. S. Osborne

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I. REVIEW OF PREVIOUS WORK

1. DETERMINATIONS PREVIOUS TO 1870

The determinations of the heat of fusion of ice up to the year 1870 have been reviewed by A. W. Smith,[1] who prepared Table 1 giving a summary of the results:

There is great variation among the results of these earlier determinations, many of them are based on but few experiments, and there is little doubt that the experiments were carried out under conditions much less favorable than for those made more recently.

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[1] Phys. Rev. 17, p. 193; 1903.

TABLE 1

Name	Date	Experiments	Temperature range of water	Heat of fusion	
				cal_{15}	Btu
Black[2]	1762	2	80–0	79.7	143.5
Wilke	....	1	72–0	72	129.6
Laplace and Lavoisier[3]	1780	2	100–0	75	135.0
Provostaye and Desains[4]	1843	17	24–10	79.1	142.4
Regnault[5]	1842	4	16–7	79.24	142.6
Regnault	1843	13	22–11	79.06	142.3
Hess[6]	1848	40	19–7	80.34	144.6
Person[7]	1850	6	16–5	80.0	144.0
Bunsen[8]	1870	2	100–0	80.02	144.0

[2] Lectures on Chemistry, Vol. I, p. 120.

[3] Mém. de l'Acad. des Sciences, 1780, p. 335; Oeuvres de Lavoisier I, p. 283.

[4] Ann. de Chim. et Phys., **8**, p. 5; 1843.

[5] Ibid., **8**, p. 19; 1843.

[6] St. Petersburg Imp. Acad. Sci. Bull. de la Classe physico-mathématique, **IX**, p. 81; 1851.

[7] Ann. Chim. et Phys., **30**, p. 73; 1850.

[8] Phil. Mag. (**41**), p. 182; 1871.

2. DETERMINATIONS SUBSEQUENT TO 1870

Smith, Arthur W.[9] (1903).

As a result of eight experiments with the purest ice Smith found for the heat of fusion 334.21 joules per gram (weighed in air against brass weights) based on the value 1.434 volts for the Clark cell at 15° C. Expressed on the basis of the present electrical units[10] and gram mass (i. e., weighings reduced to vacuo) this value becomes 333.24 joules per gram. If 4.187 joules are equivalent to one 15° calorie (see p. 255), the above result reduces to 79.59 calories per gram.

Bogojawlensky[11] (1904).

This experimenter used mercury as the calorimetric medium, employing the method of mixtures. The results of six experiments on the heat of fusion of ice range from 79.41 to 79.91 with a mean value of 79.61 calories.

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[9] See note 1, p. 235.

[10] The joule here used is defined by the ratio $\frac{e^2}{R}t$ where e is expressed in international volts and R is expressed in international ohms. The volt is based on the relation emf of Weston cell at 20° C = 1.0183 volts. The international ohm is the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross sectional area and of a length of 106.300 centimeters.

[11] Schriften der Dorpater Naturforscher Gesellschaft, **XIII**; 1904.

He also determined the specific heat of ice over the temperature range from −85° C to −5°.5 C. For reduction of the heat of fusion determinations in which the range of temperature of the ice was from −10° to 0°, he used 0.52 for the specific heat of ice.

Roth, W. A.[12] (1908).

Roth has assembled the results of a number of determinations of the density of ice and deduced a value to use in calculating the heat of fusion of ice from the data of Behn[13] and of Dieterici,[14] both of whom used the Bunsen ice calorimeter.

The density determinations reviewed are as follows:

Bunsen (Ges. Abh., **8**, p. 475), corrected value	0.9168
Zakrzevski (Ann. der Phys. (3), **47**, p. 155; 1892)	.91658
Leduc (Compt. rend., **142**, p. 149; 1906)	.9176
Nichols (Phys. Rev., **8**, p. 21; 1899)	.91603 to .91795
Barnes (Phys. Rev., **18**, p. 55; 1901)	.91649
Vincent (Phys. Rev., **15**, p. 129; 1902)	.9160

He states the mean, excluding Nichol's values, to be 0.9167, but uses Bunsen's corrected value 0.9168 on the assumption that the conditions of producing the ice used in that density determination were nearly the same as those under which the ice calorimeter is generally used.

Applying this value to Behn's data Roth obtains for heat of fusion of ice 79.69 cal_{15° similarly for Dieterici's data 79.60 cal_{15°.

A summary of the foregoing values giving the results of the most important determinations subsequent to 1870 is given in Table 2.

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[12] Zs. für Phys. Chem., **63**, p. 441; 1908.

[13] Ann. der Phys. (4), **16**, p. 653; 1905.

[14] Ibid., p. 593; 1905.

TABLE 2

Name	Date	Experiments	Heat of fusion	
			cal_{15° per gram	Btu per pound
Smith	1903	8	[15] 79.59	143.3
Bogojawlensky	1904	6	79.61	143.3
Behn (calculated by Roth)	1905	....	79.69	143.4
Dieterici (calculated by Roth)	1905	....	79.60	143.3
Mean	....	....	79.62	143.3

[15] The determinations of Smith have been recalculated to the basis of the 15° calorie and the gram mass. The remaining values are taken from the publications cited.

II. DESCRIPTION OF CALORIMETRIC METHODS AND APPARATUS

1. CALORIMETRIC METHODS

Two methods of calorimetry were employed in this work. In both methods the precision calorimeter described later was used, with calorimetric platinum resistance thermometers, water being the calorimetric medium. One was the well-known method of mixtures. The other was an electrical method somewhat resembling that of A. W. Smith, but differing from it in the use of water instead of oil as the calorimetric medium, in the form and size of ice specimens, and in the type of calorimeter and thermometers. The ice sample was put directly into the water and the approximate amount of energy required to melt the ice supplied electrically and measured, the small excess or deficiency being determined from the small rise or fall of temperature of the calorimeter. The temperature of the calorimeter water thus remained very constant, although a large amount of ice was used, and the corrections for heat interchange between calorimeter and surroundings were rendered small.

Although the electrical method as here carried out is the more precise because of the avoidance of large cooling corrections, nevertheless the ultimate accuracy with which the results can be expressed in terms of the calorie is limited by the accuracy with which the ratio of the joule to the calorie is known (at present

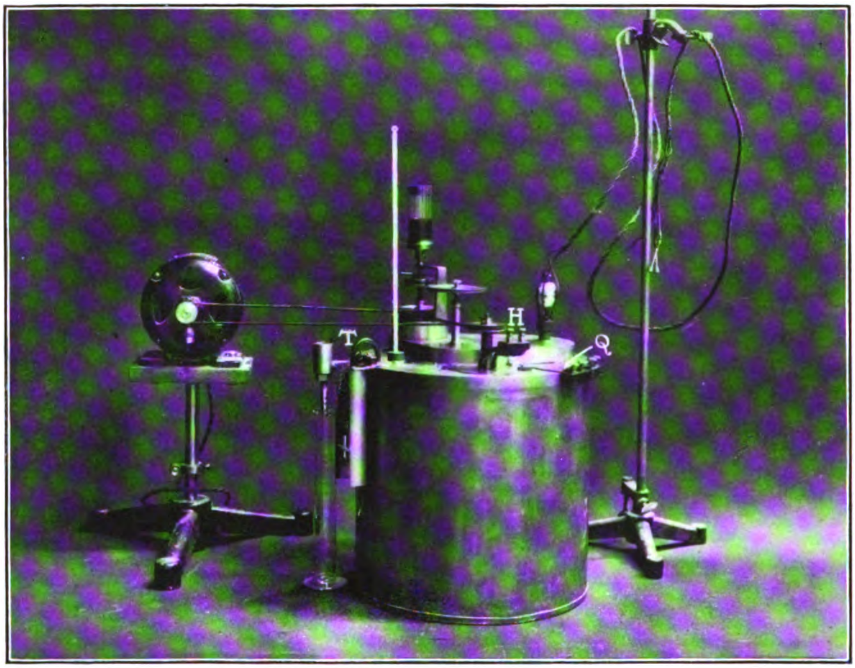

Fig. 1.—*The calorimeter, assembled as used*

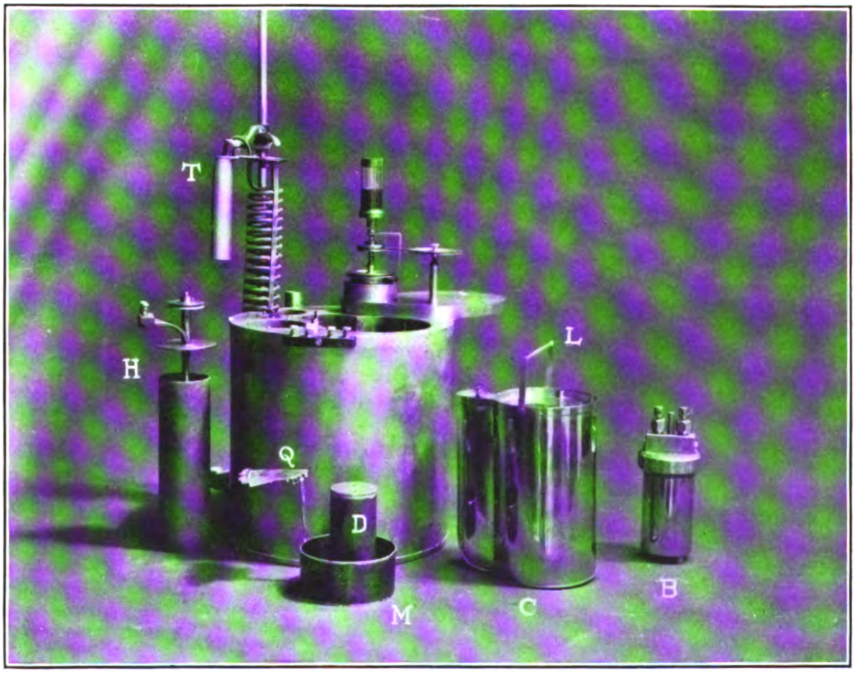

Fig. 2.—*The calorimeter, detail of parts*

probably about 1 part in 2000); and for this reason the less precise method of mixtures was used as a direct and independent check.

The methods of manipulation are described more in detail later (pp. 242–245).

2. CALORIMETER

A calorimetric outfit originally developed for use with combustion bombs, but which has proved very well adapted to various calorimetric problems, was used without modifications for the present investigation. This calorimeter is described briefly below. A more detailed description of it will be communicated in the paper cited in footnote 23, p. 260.

Fig. 1 shows the jacket and the induction motor as they appear in use.

The stirrer mounted in the cover automatically keeps water from the jacket circulating through the cover. The parabolic speed indicator mounted on top of this stirring shaft indicates the speed of stirring.

The current and potential leads to the electric heating coil are brought in across the top of the jacket inside of a closely fitting copper sheath (Q), from which they are insulated by thin mica. The sheath is in close contact with the top of the jacket and is covered with a felt pad, so that the leads will be very nearly at the same temperature as the jacket.

Terminals to the heating coil in the jacket, and the upper part of the thermostat used when necessary to maintain a constant temperature in the jacket, are also shown, marked (H) and (T).

Fig. 2 shows the jacket with its cover turned aside to admit the calorimeter, illustrating how the cover is conveniently opened and closed without interfering with the stirring in the jacket. The calorimeter proper (C), with its cover and detachable handle (L), and the heating coil (M) are shown at the right. The figure also includes a displacement buoy (D) and a combustion bomb (B) not used in these experiments. A heating coil (H) for the jacket and the thermostat (T) appear at the left.

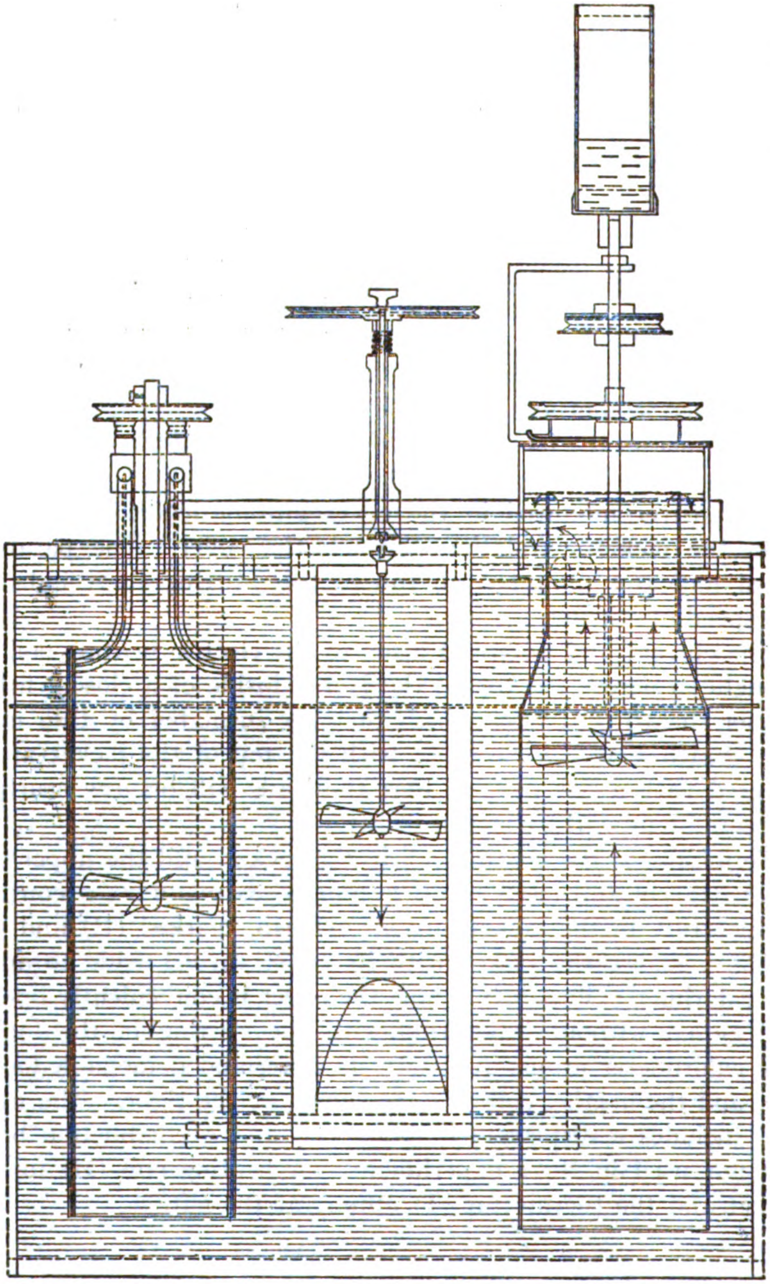

Fig. 3.—*Section through calorimeter*

Fig. 3 shows the details of construction, representing a section through the three stirring shafts. The direction of circulation of the water is indicated by arrows. The main jacket stirrer draws water from the bottom of the jacket, sending part of it through the cover, which is at a higher level than that of the water in the jacket, and allowing the remainder to overflow into the upper part of the jacket. The method of connecting the calorimeter stirrer to its shaft is also shown. The energy supplied by the stirrer is due to fluid friction only, since there is no bearing within the calorimeter.

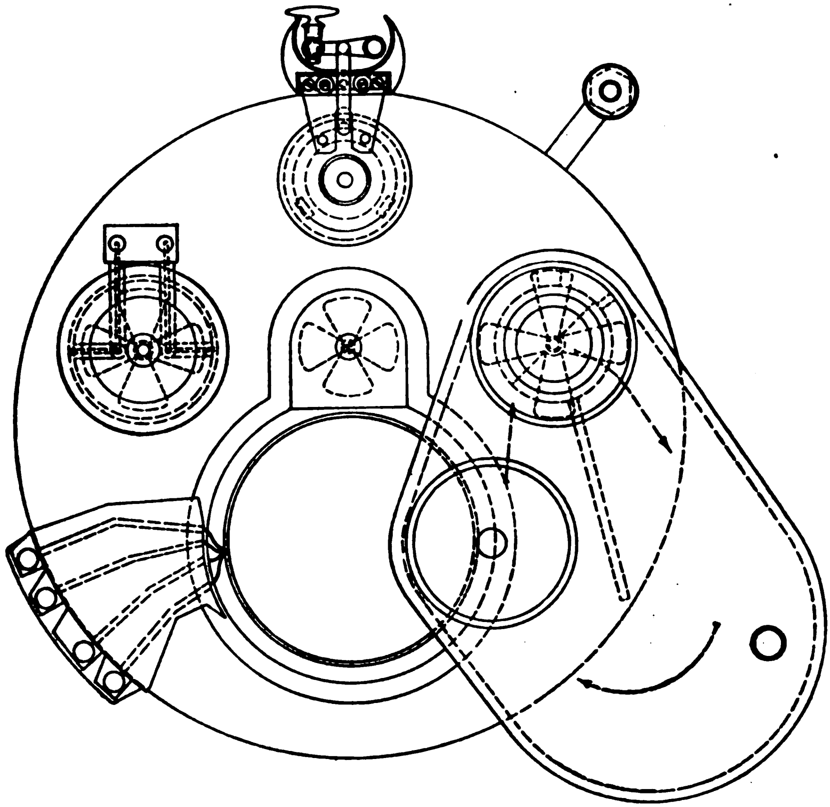

Fig. 4.—*Plan of calorimeter*

Fig. 4 is a plan of the instrument with the cover open.

There are thus realized (1) a well-stirred water calorimeter, (2) a very nearly uniform temperature jacket completely surrounding it, and (3) the absence of any material of sensible heat capacity at an intermediate temperature which could affect the rate of cooling.

Constants of the calorimeter are as follows:

Water equivalent of metal container and all fixed metal parts as used, nearly all copper, 41 grams.

Water equivalent of heating coil, 11.5 grams.

Capacity of calorimeter, 3750 cm^3.

Cooling constant 0°000030 per second per degree, or 0.115 calories per second per degree.

Variation of cooling constant with temperature, 0°000 000 2 per degree.

Power supplied by stirrer at 300 r.p.m., 0.051 watts; heats the calorimeter 0°000 000 32 per second.

Residual effect of the temperature of the room on the cooling constant, due to heat conducted by electrical lead wires, etc., past the jacket into the calorimeter, is 0.0014 calories per second per degree difference in temperature between room and jacket.

The sensitive platinum resistance thermometers used to measure the temperature of the calorimeter water have been described in detail.[16] As used they could be read to 0°0001 C and were probably accurate to 0°0003.

The difference in temperature between the calorimeter and jacket was determined by means of a copper constantan thermoelement the two junctions of which in the form of flat plates rested, one against the bottom of the calorimeter and the other against the jacket.

3. ELECTRICAL METHOD

A steady supply of energy in the calorimeter heating coil was furnished by a storage battery of 80 volts. The current was so constant that the mean value could be determined to 1 part in 20000 during the period of five, six, or seven minutes for which it was usually employed. The measurement of the energy consisted of determinations of the current, the potential difference between the coil terminals, and the duration.

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[16] Dickinson and Mueller: New Calorimetric Resistance Thermometers, this Bull., 9, p. 483; 1913.

The method of these measurements has been previously described.[17] A diagram of the circuits is shown in Figure 5. The quick break switch (S) served to throw the current into either the heating coil (M) or a rheostat (R) of equal resistance outside the calorimeter, and simultaneously to record on the chronograph tape the time when the switch was thrown. Measurements of current and potential difference were taken alternately during the period of energy supply, using the switch (K) which connects the potentiometer with either the 0.1-ohm coil or the volt box. The heating coil was of such a resistance (10 ohms) that the potentiometer settings were very nearly the same for both measurements. The mean current, mean potential difference and the time, the product of which measures the total energy, were each measured to better than 1 part in 20000.

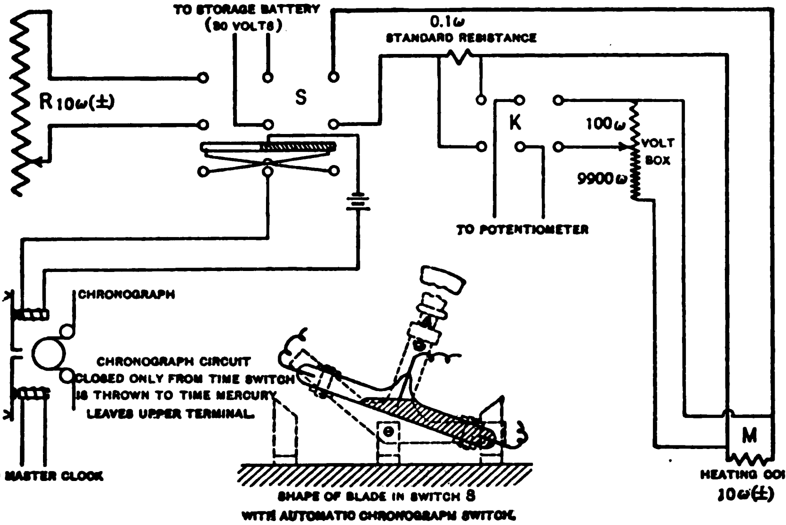
TO STORAGE BATTERY (80 VOLTS)
0.1ω STANDARD RESISTANCE
R 10ω(±)
S
K
100ω
VOLT BOX
9900ω
TO POTENTIOMETER
CHRONOGRAPH
CHRONOGRAPH CIRCUIT CLOSED ONLY FROM TIME SWITCH IS THROWN TO TIME MERCURY LEAVES UPPER TERMINAL
M
TO MASTER CLOCK
SHAPE OF BLADE IN SWITCH S WITH AUTOMATIC CHRONOGRAPH SWITCH
HEATING COIL 10ω(±)

Fig. 5.—*Diagram of circuits for electrical method*

In this method the difference in temperature of the calorimeter water before and after melting the ice was seldom more than 0°2 C. However, during the period of melting, on account of the more rapid melting of the ice sample when first introduced, the temperature of the calorimeter fell during the earlier part and rose later. (See Fig. 9.) The shape of the ice sample was chosen with a view to making the rate of melting as uniform as possible. (See p. 246.)

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[17] Dickinson, Mueller, and George: Specific Heat of Calcium Chloride Solutions, this Bull., 6, p. 379; 1910.

The mean temperature difference between calorimeter and jacket was obtained by observations on the thermoelement at half-minute intervals.

The procedure for a determination was as follows: The ice specimen of suitable shape and size was weighed approximately to determine the amount of water necessary to accommodate it in the calorimeter. This amount of water was weighed into the calorimeter, the calorimeter was put in place in the jacket, and the heating coil placed in the calorimeter. The jacket cover was then closed, the thermometer inserted, the stirrer started, and the temperature of the calorimeter adjusted to that of the jacket by use of the thermocouple. Meanwhile the ice specimen was accurately weighed and the heating current adjusted to supply the required amount of energy when flowing for a suitable integral number of minutes, so determined by preliminary experiments as to cause least variation in temperature of the calorimeter. To avoid error due to the contact device on the standard clock, the current was always thrown on and off at the same break second.

After several observations of the temperature of the calorimeter, the operations of opening and closing the jacket cover were performed in the same manner as when introducing an ice specimen and the temperature was again observed in order to determine the thermal effect of opening. This was found to be from 0°001 to 0°004 and to vary with surrounding conditions, so that as a precaution it was observed for nearly every determination.

With all in readiness the cover was opened, the specimen introduced as described later (p. 248), the heating current thrown on, the cover closed, stirrer started, and thermometer reinserted, all these manipulations taking place according to a prearranged program. One observer immediately began to take the potentiometer readings and the other took frequent readings on the thermocouple for the temperature difference between calorimeter and jacket until the temperature again became steady. Then another accurate temperature determination was made by means of several observations with the resistance thermometer.

The small change in temperature of the calorimeter, the heat loss or gain to the jacket, and the effect of opening the calorimeter are treated as corrections to the total measured energy supplied electrically.

The cooling constant, effect of stirring and lead conduction, and thermocouple sensibility were frequently determined, although the corrections due to these factors proved so small as to render this precaution almost unnecessary.

4. METHOD OF MIXTURES

In the determinations by the method of mixtures the heating coil and the apparatus for measurement of electric energy were not required. In other respects the apparatus and experimental procedure were similar to those of the electrical method except that, owing to the desirability of keeping the cooling correction within suitable limits, smaller specimens of ice (100 to 200 grams) were found better suited to the method of mixtures.

The initial temperature of the calorimeter was made slightly lower than that of the jacket and the final temperature was from 3° to 6° lower, depending upon the amount of ice melted. The temperature difference between jacket and calorimeter during the experiment was in some cases determined by the thermocouple and in others by the resistance thermometer. The cooling corrections in this method were usually of the order of 2 per cent of the total heat in question.

III. MATERIALS

The ice used for most of the determinations was commercial artificial can or plate ice frozen from city filtered water which was distilled and boiled before freezing. The samples were especially selected for clearness and freedom from bubbles. The can ice was the same as that used regularly at the Bureau of Standards for determining ice points of thermometers. Frequent conductivity tests showed it to be very pure.

For purposes of comparison, determinations were made on ice from several other sources. Natural ice, about one foot thick, from Maine was used in preparing the specimens for five of the experiments. This ice was not very clear in appearance, containing many air bubbles, but conductivity tests showed that it was nearly as pure as double-distilled water.

A number of specimens were prepared from double-distilled water frozen in a tin-lined cylindrical copper vessel constructed to give samples of the required shape and size. The water was either first boiled to remove dissolved air and then frozen as quickly as possible or else the vessel was evacuated and the water frozen while the air was excluded. These processes were not entirely successful in producing perfectly clear ice, although ice of a very good degree of clearness was obtained.

One sample was frozen from water purposely contaminated with a mixture of ammonia, sodium chloride and calcium chloride, to the extent of about 1 part in 1000.

IV. MANIPULATION OF ICE

1. MANUFACTURE OF SPECIMENS

In order to secure greater uniformity in the rate of melting than would obtain with solid blocks, specimens were made in the shape of hollow circular cylinders of about 9.5 cm outside diameter and from 2 to 4 cm inside diameter. The lengths varied from about 3 cm to 9.5 cm. Fig. 6 shows a photograph of two of the specimens in the copper holders.

In making the specimens from commercial ice a rectangular piece was first sawed from the selected solid block. By planing with an ordinary ice shaver this was worked down to a cylinder of the required diameter, which was then sawed into the lengths desired. A hole was drilled through the principal axis of each specimen and enlarged to proper size by running tap water. A few of the specimens, which were dried mechanically at the melting point, were left solid. The ice which was frozen in the cylindrical copper can was obtained in the form of a hollow cylinder and required only to be sawed into the desired lengths.

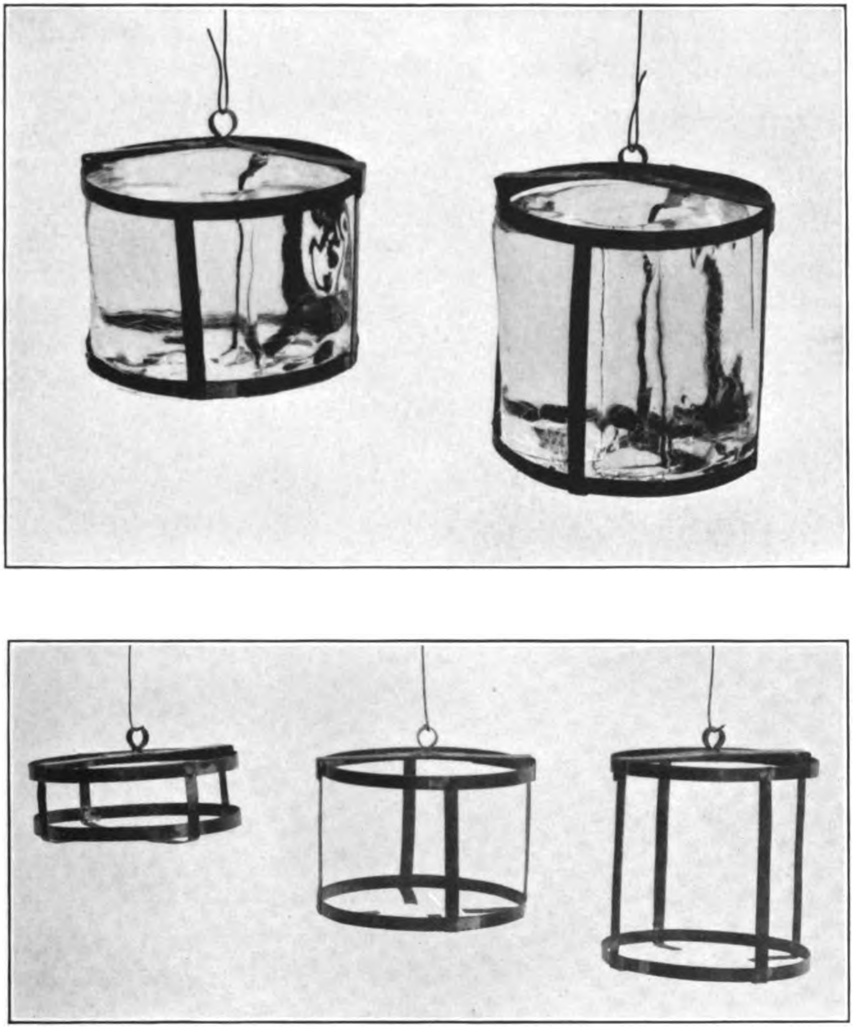


Fig. 6.—*Ice specimens, showing hollow cylindrical shape employed. Copper holders for the specimens*

2. PRECOOLING THE SPECIMENS

DESCRIPTION OF CRYOSTATS

In order to insure the dryness of the ice, except for the few specimens which were mechanically dried, and to bring the specimens to a definite temperature before the determination, two *cryostats* were used. One of these cryostats is shown in section in Fig. 7. The cylindrical copper vessel (A) is supported within a larger cylindrical vessel externally insulated by cork chips (C) within a wooden box. The space (B) between the two vessels is packed solidly with a cryohydric mixture of finely shaved ice, a suitable salt, and saturated aqueous solution of the salt. The top of the vessel (A) is covered with a removable vessel (E), also filled with the cryohydric mixture. A tube extends through this cover to admit the suspension hook (G) used in weighing the specimens. The insulating covers (D) and (F) are removable.

The other cryostat was similar in construction, but had somewhat thicker insulation and lacked the central tube in the removable cover. The one is called the weighing cryostat and the other the storage cryostat. Three specimens could be accommodated in the storage cryostat and two in the weighing one, as shown.

For a day's series of determinations, the specimens were placed in the cryostats the previous afternoon, allowing at least 16 hours for the specimens to come to a constant temperature before the determinations were made. The salts employed were boric acid and magnesium sulphate, U.S.P. purity.

3. TEMPERATURE OF CRYOSTATS

For determining the temperature attained in the cryostats, surveys by means of copper-constantan thermoelements were made. Single junctions at various points on the interior wall of the cryostat were each connected to a reference junction kept in ice. The thermo electromotive force was measured by a potentiometer, and although the sensibility was a fraction of a microvolt, the accuracy of the temperatures may not have been better than 0°05 C, on account of the fact that the thermoelements were not rigidly inclosed and possibly not always immersed to the same depth.

The temperature uniformity of the interior walls was found to be better in the storage cryostat than in the weighing one, both as to vertical distribution and constancy with time.

Further test as to the temperature assumed by an ice specimen in the cryostats was made by inserting four junctions directly into holes drilled in the ice. The holes were then filled with water, plugged up, the water frozen and the specimen placed in the cryostat as when preparing for a determination. It was found that a specimen thus prepared and put in the cryostat at 4 p. m. attained by 9 a. m. next day an equilibrium temperature condition within the accuracy of the tests referred to above.

Transfer of the specimen from the storage cryostat to the weighing one produced a small rise of temperature which persisted while the specimen was kept in the weighing cryostat. The change is therefore doubtless due to the slightly higher average temperature of this cryostat, owing partly to the smaller cover vessel and partly to the central tube through the cover. As a result of these surveys the temperature of the specimens either cooled in the storage cryostat with the boric acid mixture and then transferred to the weighing cryostat, or else cooled in the later was found to be $-0\overset{\circ}{.}72$ C. With the magnesium sulphate mixture the observations showed that the temperature of the specimen should be taken as $-3\overset{\circ}{.}78$ C.

4. HANDLING THE SPECIMENS

For handling the specimens, when packing them in the cryostats, weighing, and transferring to the calorimeter, they were inclosed in holders made of sheet copper, as shown in Fig. 6. The bar across the top which carries the supporting ring is detachable for inserting the specimen. Each was provided with a loop of linen thread passed through the ring, by means of which the specimen could be transferred to the weighing cryostat and then lifted until the suspension hook was engaged in the ring. The thread was then cut and removed, leaving the specimen hanging, as shown in Fig. 7. After weighing, the specimen was transferred to the calorimeter by lifting the cover vessel, suspension hook, and specimen together from the cryostat, carefully lower-

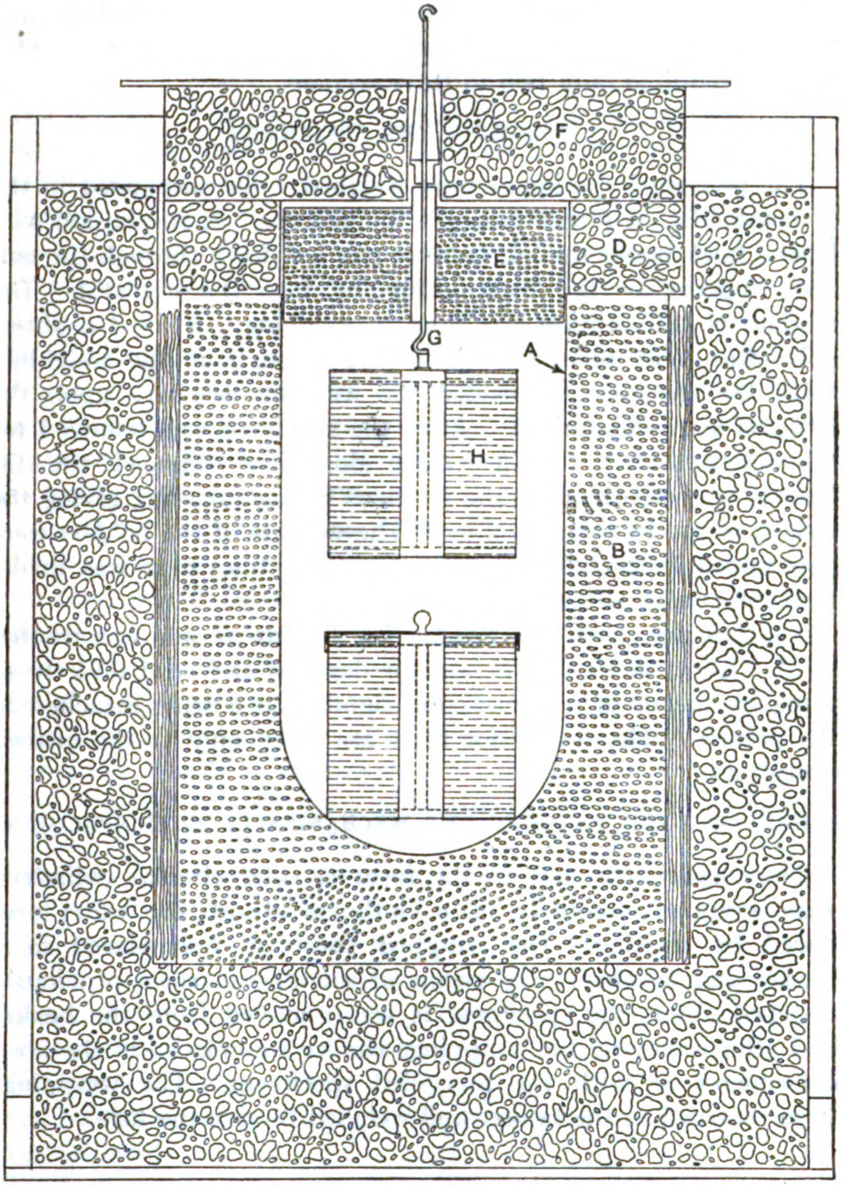


Fig. 7.—*Section through cryostat, by use of which ice specimens were brought to a fixed, known temperature*

ing the specimen into the open calorimeter, and then detaching the hook, leaving the specimen immersed in the water. This transfer required only two to three seconds.

5. WEIGHING THE SPECIMENS

The precooled specimens were weighed while suspended in the cryostat (Fig. 7) placed beneath the balance. A suspension wire from a hook under the left balance pan led down through the balance support to the hook extending into the cryostat. The method of substitution was used in weighing. A fixed counterpoise was kept upon the right pan throughout the weighing. With the specimen suspended the weights necessary upon the left pan were determined. After the specimen was removed for the determination, the suspension alone was balanced, the difference between this and the previous balance reading giving the weight of specimen and holder. The weights of the holders were determined separately. Correction for air buoyancy was made, thus the results are expressed in mass units.

The balance used in weighing ice specimens was constructed by A. Collot, of Paris. It was air damped and read directly to 1 mg by means of a microscope sighted on a scale attached to the pointer. The results for mass are given only to the nearest centigram.

6. HANDLING AND WEIGHING THE MECHANICALLY DRIED SPECIMENS

These specimens, cut in the form of solid circular cylinders, were wrapped loosely in linen cloths to absorb the water produced by melting. The wrapped specimen was placed in a beaker and weighed. By means of a copper harness previously fastened about the specimen, it was removed from the beaker and after removing the wrappings the ice was placed in the open calorimeter as with the precooled specimens. The wrappings were returned to the beaker and weighed to give the tare.

V. CALCULATION OF EXPERIMENTAL RESULTS

1. ELECTRICAL METHOD

The method of making the calculations will be explained with reference to the sample laboratory record forming Fig. 8: t_1 and t_2 are two arbitrarily selected times for which it is desired to determine as exactly as possible the corresponding calorimeter temperatures, the former before the ice is introduced, the latter soon after the ice has melted when equilibrium has again been established.

In the example t_1 is taken as 11–01–44. The data obtained previous to this instant serve to determine the temperature at t_1 which is measured by the resistance ($R_{1\ \mathrm{cor.}}$) of the platinum thermometer. These data include a series of thermometer readings from 10–58 to 11–01 which are extrapolated to 11–01–44 and corrected for the temperature change of the calorimeter which results from opening it (at about 11–01–30) to receive the ice. They also include the readings appertaining to a "blank" opening and closing, similar in all respects to the one just mentioned, from which the correction for opening is computed. The steps of the process are set forth on the sample record, and the condition at t_1 = 11–01–44 may be thus recapitulated: The calorimeter is open ready to receive the ice and the supply of electrical energy, and its temperature, corrected for everything including the effect of opening, corresponds to the value $R_{1\ \mathrm{cor.}} = 26.68404$.

Similarly, choosing t_2 as 11–09–00, the data determined after this time fix $R_{2\ \mathrm{cor.}} = 26.69160$. This is obtained by extrapolation of the series of readings from 11–11 to 11–20.

Let us now consider the heat changes in the calorimeter system between 11–01–44 and 11–09–00. There are five possible sources of energy supply to the calorimeter:

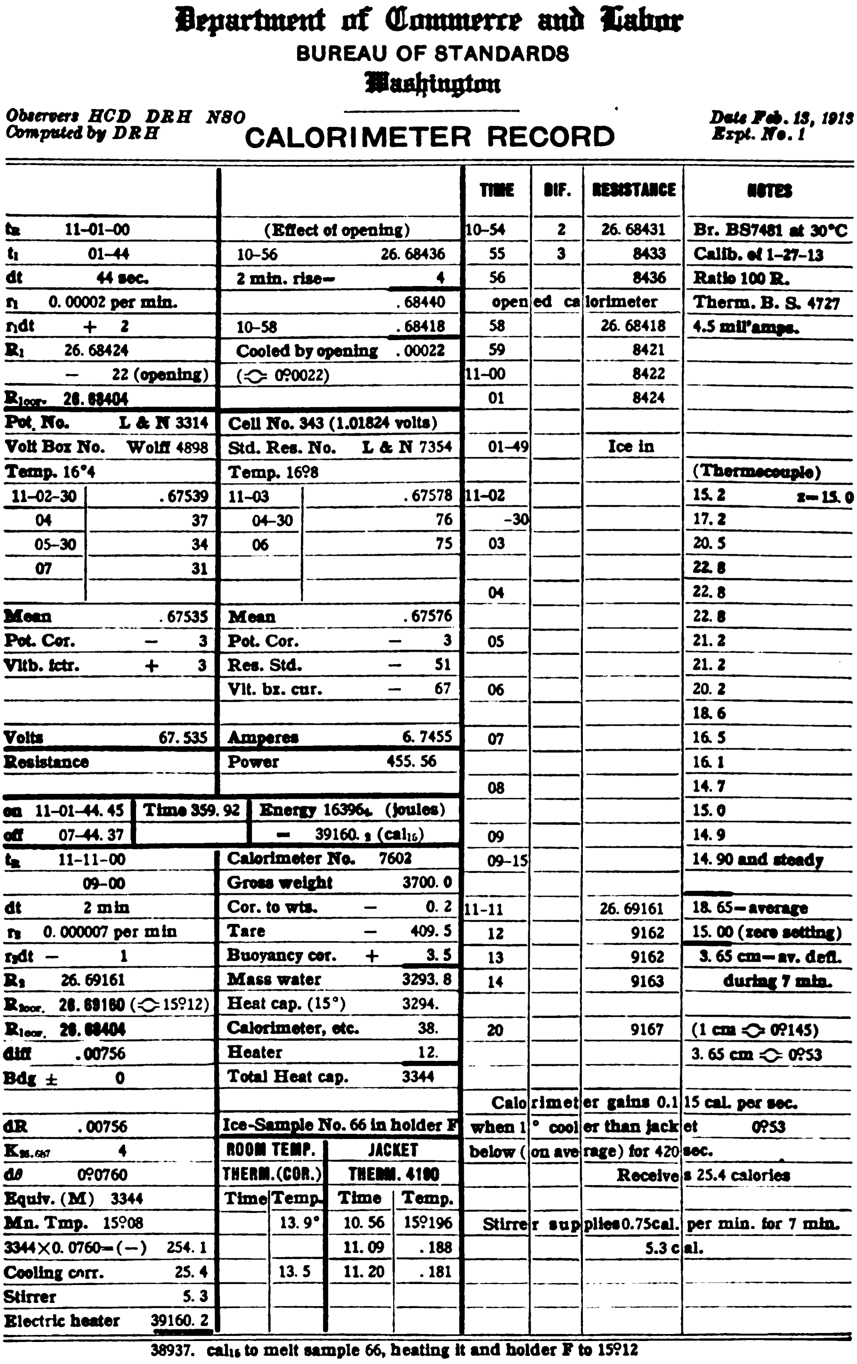
(1) Electric heating coil.

(2) Radiation, convection, etc., from jacket.

(3) Stirrer.

(4) Heat conduction through the jacket from the room (along the resistance thermometer leads, etc.).

(5) Measuring current in the thermometer.



Department of Commerce and Labor
BUREAU OF STANDARDS
Washington

Observers HCD DRH NSO
Computed by DRH

CALORIMETER RECORD

Date Feb. 13, 1913
Expt. No. 1

						TIME	DIF.	RESISTANCE	NOTES
t_a	11-01-00	(Effect of opening)				10-54	2	26.68431	Br. BS7481 at 30°C
t_1	01-44	10-56	26.68436			55	3	8433	Calib. of 1-27-13
dt	44 sec.	2 min. rise—	4			56		8436	Ratio 100 R.
r_1	0.00002 per min.		.68440			open	ed ca	lorimeter	Therm. B. S. 4727
$r_1$dt	+ 2	10-58	.68418			58		26.68418	4.5 mil'amps.
R_1	26.68424	Cooled by opening	.00022			59		8421	
	— 22 (opening)	(≎ 0°0022)				11-00		8422	
$R_{1corr.}$	26.68404					01		8424	
Pot. No.	L & N 3314	Cell No. 343 (1.01824 volts)							
Volt Box No.	Wolff 4898	Std. Res. No.	L & N 7354			01-49		Ice in	
Temp. 16°4		Temp. 16°8							(Thermocouple)
11-02-30	.67539	11-03	.67578			11-02			15.2 z—15.0
04	37	04-30	76			-30			17.2
05-30	34	06	75			03			20.5
07	31								22.8
						04			22.8
Mean	.67535	Mean	.67576						22.8
Pot. Cor.	— 3	Pot. Cor.	— 3			05			21.2
Vltb. fctr.	+ 3	Res. Std.	— 51						21.2
		Vlt. bx. cur.	— 67			06			20.2
									18.6
Volts	67.535	Amperes	6.7455			07			16.5
Resistance		Power	455.56						16.1
						08			14.7
on	11-01-44.45	Time 359.92	Energy 16396$_4$ (joules)						15.0
off	07-44.37		— 39160.$_2$ (cal$_{15}$)			09			14.9
t_2	11-11-00	Calorimeter No.	7602			09-15			14.90 and steady
	09-00	Gross weight	3700.0						
dt	2 min	Cor. to wts.	— 0.2			11-11		26.69161	18.65—average
r_2	0.000007 per min	Tare	— 409.5			12		9162	15.00 (zero setting)
$r_2$dt	— 1	Buoyancy cor.	+ 3.5			13		9162	3.65 cm—av. defl.
R_2	26.69161	Mass water	3293.8			14		9163	during 7 min.
$R_{2corr.}$	26.69160 (≎ 15°12)	Heat cap. (15°)	3294.						
$R_{1corr.}$	26.68404	Calorimeter, etc.	38.			20		9167	(1 cm ≎ 0°145)
diff	.00756	Heater	12.						3.65 cm ≎ 0°53
Bdg ±	0	Total Heat cap.	3344						
						Calo	rimet	er gains 0.1	15 cal. per sec.
dR	.00756	Ice-Sample No. 66 in holder F				when 1	° cool	er than jack	et 0°53
$K_{33.667}$	4	ROOM TEMP.		JACKET		below (	on ave	rage) for 420	sec.
$d\theta$	0°0760	THERM.(COR.)		THERM. 4180				Receive	s 25.4 calories
Equiv. (M)	3344	Time	Temp.	Time	Temp.				
Mn. Tmp.	15°08		13.9°	10.56	15°196	Stirre	r sup	plies 0.75cal.	per min. for 7 min.
3344×0.0760=(—)	254.1			11.09	.188			5.3 c	al.
Cooling corr.	25.4		13.5	11.20	.181				
Stirrer	5.3								
Electric heater	39160.2								

38937. cal$_{15}$ to melt sample 66, heating it and holder F to 15°12

Fig. 8.—*Laboratory record of an experiment by the electrical method*

Record for ice samples gives for No. 66

Initial temperature −0°.72. Weighed in holder F

Readings of Balance, 271.646 + sample + holder + suspension = counterpoise
(grams) 717.622 + suspension = counterpoise

445.976 = weight of sample and holder (in air at 0°)
37.873 = weight of holder

408.103 = weight of sample (in air at 0°)
.51 (Buoyancy correction)

408.61 = Mass of Ice

(continued from Fig. 8)

Holder F

Weight	Mean spec. ht.	Temp. Change
37.9g	0.92	−0°.7 to +15°.1

37.9×0.92×15.8 = 55

38937 (Ice and holder)
55 (holder)

38882 (Ice, 408.61g)

95.15 cal per gram
To heat 1g water from 0° to 15°.12 15.17 cal

79.98
To heat 1g ice from −0°.72 to 0° .37

79.61 = Latent heat of Fusion

Some of these sources may be sinks, which can readily be taken into account by the use of the negative sign when necessary.

The energy so supplied may go to—

(6) Heating the ice to 0°, melting it and heating the resulting water to the final calorimeter temperature.

(7) Heating the copper holder of the ice specimen.

(8) Raising the temperature of the calorimeter.

(9) Evaporating water from the calorimeter.

The last two may be negative, depending on the conditions. No ambiguity arises, however, from the more or less arbitrary division which has been made. It is assumed that these nine processes alone take place, and that when they have all been considered, all the energy changes will be accounted for. It may be shown that (4), (5), and (9) were probably less than one ten-thousandth part of (1) in all of the experiments. They were therefore neglected in making the reductions. The remaining six terms are computed in full on the records pertaining to each experiment.

Lead Conduction (4).—The calorimeter and jacket were usually a degree or two warmer than the room, but never more than 4°. The heat which reaches the calorimeter due to imperfect jacketing being 0.0014 calories per second per degree difference of temperature, a maximum of 3 calories might be introduced under the most unfavorable conditions, which is to be compared with the 30000 to 40000 calories required to melt the ice.

Thermometer Current (5).—The average current employed was 4.5 milliamperes and the thermometer resistance was about 27 ohms, so that the effect of this supply of energy on the temperature of the calorimeter would be absolutely inappreciable even were the thermometer circuit closed all the time.

Evaporation (9).—The large value of the latent heat of vaporization of water involves an appreciable quantity of energy in the evaporation or condensation of but a few milligrams, and unless the procedure be carefully planned serious error may result. A somewhat extended investigation into the evaporation from and condensation on calorimeter surfaces has been carried out in the laboratories of the Bureau of Standards and will be published in a separate communication. From the results, it is sufficient to note here that although the top water surface of the calorimeter remained uncovered, in order that the ice might be introduced quickly and without spilling water, the procedure was such that probably no error in excess of 1 part in 10000 was introduced.

Electrical Energy (1).—The data for this are collected in the left central portion of the sample record. The process of securing the readings is described on page 242. By reference to figure 5 it may be seen that the potentiometer readings, corrected for instrumental error by certificate of calibration (Pot. cor. on record sheet) give directly the potential drop across the 100-ohm section of a 10000-ohm volt box, and that across the terminals of a 0.1-ohm resistance standard. Correction for the volt-box factor, nominally 100, reduces the one set of readings to the actual voltage across the terminals of the heating coil in the calorimeter. Correction for the exact resistance of the 0.1-ohm standard reduces the other set to the current in amperes through the standard. This is the sum of the currents in the heater (10 ohms) and the volt box (10000 ohms) and the volt-box current, approximately 0.001 part of the whole, must be subtracted so as to get the current in the heating coil.

The product of the average value of the current and the emf during the period of heating is labeled "power." The quotient, the resistance of the heater coil, furnishes a valuable check against certain errors. The time factor, obtained from automatic chronograph record explained on page 243, is multiplied by the power and the product marked "energy." The unit is the joule.[18]

At this point it is necessary to introduce the value of the mechanical equivalent of heat. After careful consideration of the published values and of a considerable amount of work done in this same calorimeter at the Bureau of Standards, but not yet published, the authors have used the value 4.187 international joules equal to one 15° cal.[19]

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[18] See footnote 10 on p. 236.

[19] Some modification of the results announced in this paper will be necessary if conclusive evidence shall later indicate a value of "J" different from 4.187, but it seems very improbable that such change will exceed 1 part in 2000.

Radiation and Convection from Jacket (2).—During the period that the ice was melting the temperature difference between the calorimeter and jacket was directly indicated by a thermoelement. The readings every half minute (zero setting 15) show that the calorimeter temperature dropped steadily below that of the jacket (see Fig. 9) to a point where the galvanometer deflection was 7.8 cm, equivalent to 1.1°, held steady for about a minute, and then recovered steadily to the jacket temperature. The average deviation, the time and the cooling constant[20] of the calorimeter are set forth in order, and show the method of computing the quantity of heat involved in this correction.

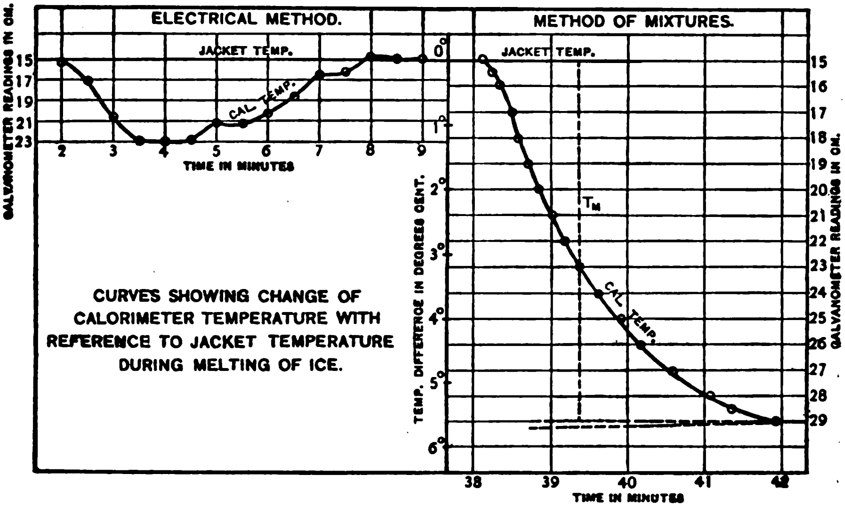

Fig. 9

Stirring (3).—The stirring was very constant as shown by the parabolic speed indicator mentioned before, and the power supply of 0.051 watts at the speed employed has been measured many times during the use of the calorimeter. This figure is equivalent to 0.73 calories per minute. The rest of the computation on the sheet requires no further explanation.

Heating of Calorimeter (8).—Any excess of energy above that absorbed by the ice and its holder will serve to raise the temperature of the calorimeter and a deficiency will be supplied by the lowering of this temperature. The quantity of heat so involved is obtained from the product of the heat capacity of the calorimeter (without the ice) by the temperature change.

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[20] Value given on p. 242.

The heat capacity, including the water and the metal parts of the calorimeter, was determined in other experiments to an accuracy of a few parts in 10000, but an accuracy of one in a thousand is more than ample for the largest value of this correction term, and figures are therefore rounded off to convenient values.

The temperature change of the calorimeter is determined from the readings $R_{1\ \mathrm{cor.}}$, $R_{2\ \mathrm{cor.}}$ In the example, $R_{2\ \mathrm{cor.}}-R_{1\ \mathrm{cor.}}$ equals 0.00756 ohms. For thermometer 4727, 0.1 ohm is about a degree, or more exactly, 1 ohm equals 10°.0459 at mean R of 26.687 ohms.[21]

$R_{2\ \mathrm{cor.}}-R_{1\ \mathrm{cor.}}$ is, therefore, equivalent to 0°.0760.

Result of an Experiment (6).—The processes tabulated on pages 251, 254 may be collected in the following statement: The electrical energy, plus that received from the jacket plus that supplied by stirring, less the amount necessary to raise the temperature of the calorimeter, is the amount of energy which goes into the ice and its holder. The weight of this holder, multiplied by its rise of temperature and its mean specific heat, gives the heat absorbed by the holder (7). The remainder of the heat, divided by the mass of ice, gives a value for the total heat of 1 gram from the initial temperature of the ice to the final calorimeter temperature ($R_{2\ \mathrm{cor.}}$). The total heat of 1 gram of water from 0° to the temperature $R_{2\ \mathrm{cor.}}$ (in terms of the 15° calorie) is computed from the results of Professor Callendar's [22] recent work.

Should the values given by Callendar be in error to the extent of 1 part in 1000, it would affect the results of this paper by about 1 part in 4000.

The heat required to change 1 gram of ice at an initial temperature below 0° to water at 0° can not be reduced to give a value for the latent heat of fusion of ice without a knowledge of the specific heat of ice. The discrepancies found in existing data on this constant are so great as to render it very desirable that an early redetermination be made with suitable apparatus and methods, and the Bureau is now engaged in doing this.

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[21] Reduction by method described in paper cited in footnote 17, p. 242.

[22] Phil. Trans. Royal Society, London, **212A**, p. 1; 1912.

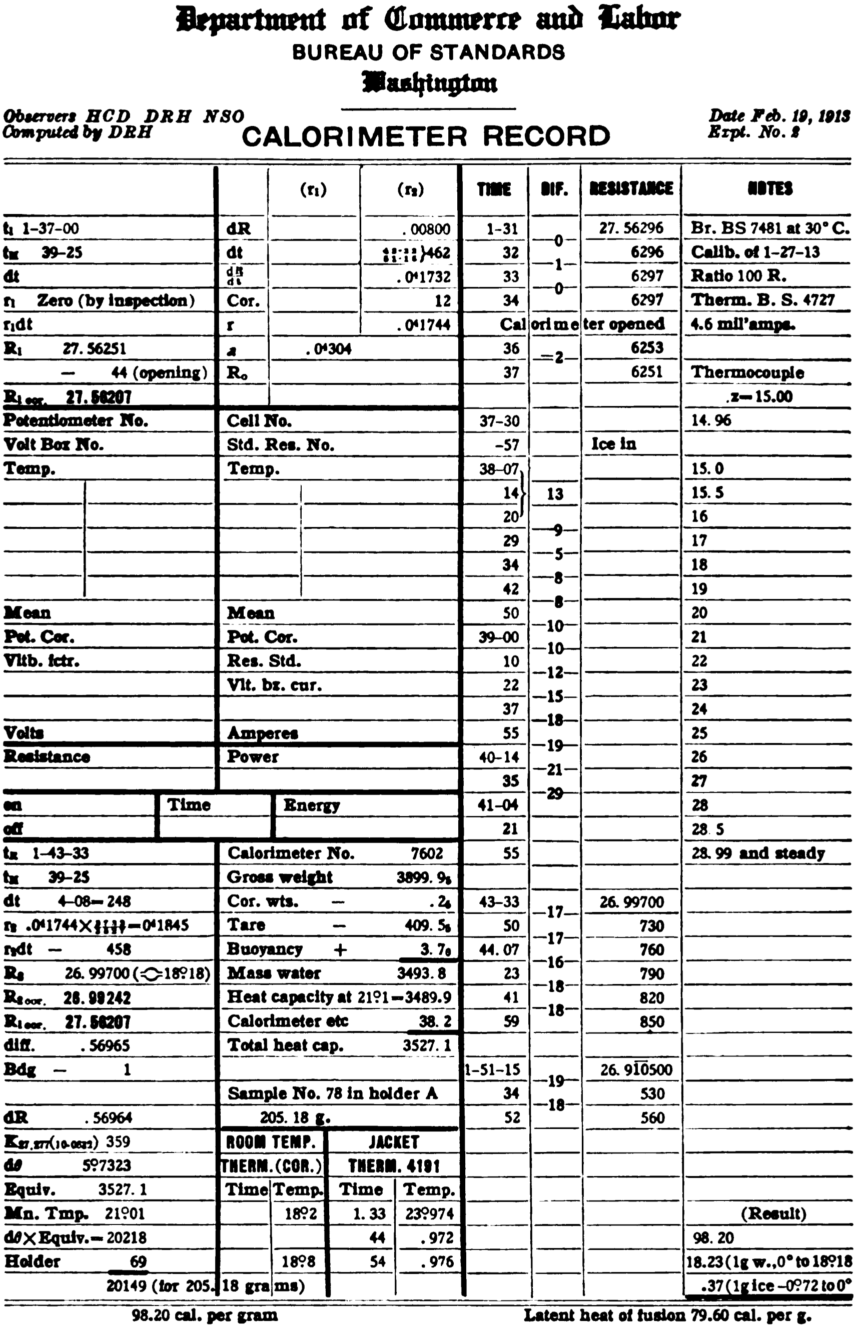
For the determinations at $-0\overset{\circ}{.}72$ an approximate value of the specific heat of ice will suffice. The figure 0.52 is here used. An error of 4 per cent in this constant affects the result by about 1 part in 4000. For the determinations at $-3\overset{\circ}{.}78$, an error of 4 per cent in the assumed value of $0\overset{\circ}{.}52$ will affect the result to the extent of 1 part in 1000.

2. METHOD OF MIXTURES

In this method most of the heat required to melt the ice and raise the temperature of the resulting water to the final calorimeter temperature comes from the cooling of the water originally in the calorimeter. Therefore the amount of cooling and the heat capacity of the system require exact determination, while all the other terms entering the computation are relatively small and permit of more or less approximation. The cooling correction is very much larger than in the electrical method, being 1 to 2 per cent of the total heat measured.

A sample laboratory record of an experiment by this method forms Fig. 10. It is similar to Fig. 8, the notation employed is the same, and the general method of making reductions differs only in so far as different magnitudes for the terms make this necessary. The selections of times t_1 and t_2 and the fixing of the corresponding temperatures as measured by resistances R_1 and R_2, follow exactly the description of p. 251 which need not be repeated here.

Between the times t_1 and t_2 the same nine processes which are tabulated on pp. 251-254 occur, except that (1) is missing, and (8) is always a cooling of the calorimeter, the major term of the computation referred to above; (2) and (3) will be discussed together, below. Terms (4) and (5) were negligible, and also (9), the remarks on p. 254 concerning their magnitude applying also to the experiments by the method of mixtures. The calculations involved in paragraphs numbered (6) and (7) are identical in the two methods, so that for the purpose of illustrating the reduction of a method of mixtures experiment it is unnecessary to retain in Fig. 10 the complete detail that is shown in Fig. 8, beyond the computation of the total heat absorbed by the ice.



Department of Commerce and Labor

BUREAU OF STANDARDS

Washington

Observers HCD DRH NSO
Computed by DRH

CALORIMETER RECORD

Date Feb. 19, 1913
Expt. No. 2

		(r_1)	(r_2)		TIME	DIF.	RESISTANCE	NOTES
t_1 1-37-00	dR		.00800		1-31	0	27.56296	Br. BS 7481 at 30° C.
t_{II} 39-25	dt		[illegible] 462		32	1	6296	Calib. of 1-27-13
dt	$\frac{dR}{dt}$		$.0^41732$		33	0	6297	Ratio 100 R.
r_1 Zero (by inspection)	Cor.		12		34		6297	Therm. B. S. 4727
$r_1$dt	r		$.0^41744$		Cal	orime	ter opened	4.6 mil'amps.
R_1 27.56251	a	$.0^4304$			36	=2	6253	
— 44 (opening)	R_0				37		6251	Thermocouple
$R_{1\,cor.}$ 27.56207								.z=15.00
Potentiometer No.	Cell No.				37-30			14.96
Volt Box No.	Std. Res. No.				-57		Ice in	
Temp.	Temp.				38-07			15.0
					14	13		15.5
					20	9		16
					29	5		17
					34	8		18
					42	8		19
Mean	Mean				50	10		20
Pot. Cor.	Pot. Cor.				39-00	10		21
Vltb. fctr.	Res. Std.				10	12		22
	Vlt. bx. cur.				22	15		23
					37	18		24
Volts	Amperes				55	19		25
Resistance	Power				40-14	21		26
					35	29		27
on	Time	Energy			41-04			28
off					21			28.5
t_{II} 1-43-33	Calorimeter No.	7602			55			28.99 and steady
t_{II} 39-25	Gross weight	3899.9_8						
dt 4-08=248	Cor. wts. —	$.2_4$			43-33	17	26.99700	
r_2 $.0^41744\times$[illegible]$=0^41845$	Tare —	409.5_8			50	17	730	
$r_2$dt — 458	Buoyancy +	3.7_0			44.07	16	760	
R_2 26.99700 (⌒18°18)	Mass water	3493.8			23	18	790	
$R_{2\,cor.}$ 26.99242	Heat capacity at 21°1=3489.9				41	18	820	
$R_{1\,cor.}$ 27.56207	Calorimeter etc	38.2			59		850	
diff. .56965	Total heat cap.	3527.1						
Bdg — 1					1-51-15	19	26.9$\overline{10}$500	
	Sample No. 78 in holder A				34	18	530	
dR .56964	205.18 g.				52		560	
$K_{27.277}(10.0632)$ 359	ROOM TEMP.		JACKET					
dθ 5°7323	THERM. (COR.)		THERM. 4191					
Equiv. 3527.1	Time	Temp.	Time	Temp.				
Mn. Tmp. 21°01		18°2	1.33	23°974				(Result)
dθ×Equiv.=20218			44	.972				98.20
Holder 69		18°8	54	.976				18.23 (1g w., 0° to 18°18
20149 (for 205.18 grams)								.37 (1g ice −0°72 to 0°

98.20 cal. per gram

Latent heat of fusion 79.60 cal. per g.

Fig. 10.—*Laboratory record of an experiment by the method of mixtures*

The fundamental equation of the method of mixtures as applied to these experiments may be stated in the following terms: The heat absorbed by the ice and holder is equal to that given up by the calorimeter in cooling plus that received from the jacket by radiation, convection, etc., plus that supplied by the stirrer.

The heat exchange between the jacket and the calorimeter may be computed as a quantity of heat, as was done in reducing the observations by the electrical method, or it may be expressed in terms of the temperature change in the calorimeter which this quantity of heat would cause. When the data upon which the computation is based are obtained by observing rates of rise or fall of the calorimeter temperature, it is usually more convenient to adopt the latter method. A number of methods of making the computation have been devised and might have been followed in this reduction; the one actually employed is described in detail elsewhere.[23] The computation proceeds with the aid of a mean time, (T_m), the value of which is dependent on the readings of the temperature difference between calorimeter and jacket during the period t_1 to t_2. The details are very easily carried out, but the explanation is somewhat tedious and the reader interested is referred to the paper cited. The result is comprised in the sum of the terms r_1dt and r_2dt of Fig. 10, 458 parts in 57000 for this particular example. (This result may be checked by employing the observation data of the sheet with any method of computing a cooling correction.)

The large change in the heat capacity of the calorimeter during the course of the experiment, by reason of the introduction of the ice, complicates the process somewhat.

The method of computation automatically corrects for the heat supplied to the calorimeter by the stirrer, provided this supply takes place at a constant rate.

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[23] H. C. Dickinson: Combustion Calorimetry and the Heats of Combustion of Sugar, Benzoic Acid, and Naphthalene, to be published in this Bulletin.

The temperature change [24] of the calorimeter was computed as follows: The difference of the resistance readings R_2 and R_1 was first corrected, by certificate of calibration, for error in the Wheatstone bridge used to measure the resistances. The corrected resistance difference, dR, was then reduced to centigrade temperature difference, dθ, by employing a factor [25], K, appertaining to the thermometer used. This factor, 10.0632 in the example, was convenient for slide rule computation, the term 0.56964 being increased by 632 parts per 100000 of itself.

The heat capacity of the calorimeter was determined from the mass of water employed and the heat capacity of the metal parts. Fig. 10 shows the mass determination in detail. This mass was multiplied by the ratio of the heat capacity of water at the mean temperature of the experiment to the heat capacity at 15°. The figure employed for the ratio was that given by Callendar.[26] The heat capacity of the metal parts was computed from the weights recorded when the calorimeter was built and the specific heats. For copper 0.92 was employed for this constant. An error of 1 per cent in this factor affects the total heat capacity of the calorimeter to the extent of 1 part in 10000.

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[24] The scale of temperature (t) to which these measurements are referred is related to the so-called platinum temperature

$$P_t = \frac{R_t - R_0}{R_{100} - R_0} 100$$

by the equation

$$t - P_t = 1.48 \left(\frac{t}{100} - 1\right) \frac{t}{100}$$

The thermometric scale thus defined is in agreement with the International Hydrogen Scale, from which the constants were indirectly determined as explained in this Bulletin, 3., p. 441; 1907, to the accuracy with which this scale has been reproduced at the Bureau of Standards (Bulletin 3., p. 663). However, the scale here used is more accurately reproducible than is the International Hydrogen Scale, by the use of the above formulas, applied to thermometers of equally pure platinum.

Thermometers made with this platinum have the following characteristics: Coefficient $\frac{R_{100} - R_0}{R_0} = 0.391$ to 0.392 and the constant (1.48 in the foregoing equations) equals about 1.49 when determined from observations in ice, steam and sulphur vapor (444.5 °C.).

[25] See footnote 21 on p. 257.

[26] See footnote 22 on p. 257.

VI. RESULTS

All together the heat of fusion of 92 individual ice samples has been determined by one of the two methods. Of these, the first 50 determinations were made on samples cooled in cryostats antedating those described in this paper, in which the temperatures and the distribution of temperature were not so well known. These observations, which include commercial plate, can, and natural ice as well as ice frozen in the laboratory from double-distilled water both free from air and containing air, showed no differences greater than one part in a thousand in the heat of fusion for these various samples. However, on account of the uncertainty in the initial temperature of the ice, these earlier determinations are entitled to little or no weight in fixing the absolute value of the latent heat of fusion of ice. The results are therefore omitted from this paper.

Four observations on samples of ice artificially contaminated with a mixture of equal parts of ammonia, sodium chloride, and calcium chloride, to the extent of about one part in a thousand, gave results about 1.4 per cent lower than for pure ice.

Of the remaining observations, summarized in Tables 3, 4, and 5, 14 were made with specimens cooled to $-3^\circ.78$, thus bringing in a considerable uncertainty because of the lack of accurate information as to the specific heat of ice. A comparison of these results with those on samples cooled to $-0^\circ.72$ serves to give an approximate value for this constant, and the results can hardly be considered as of value other than for such comparison until more accurate determinations of the specific heat of ice are available for their reduction.

The mean of 12 observations by the electrical method on specimens initially at $-3^\circ.78$ is 81.61, for the total heat from $-3^\circ.78$ to water at 0°. Similarly, the mean of 15 observations by the same method on samples initially at $-0^\circ.72$ is 80.02. A comparison of these figures gives for the specific heat of ice 0.520, a value which is in good agreement with the number previously selected as representing the most probable value of this constant. This value is taken for reducing the results of the 21 observations upon which is based the final value of the heat of fusion.

The results which are given in Tables 3, 4, and 5 may be summarized as follows:[37]

TABLE 3

Summary of Experiments by Electrical Method (Ice at −0°.72)

Date	Sample and source	Mass Ice (grams)	Elect. Energy +4.187	M×dθ (cal.)	Cooling cor. (cal.)	Stir. (cal.)	Holder (cal.$_{15}$)	Ice, −0°.72 to Water, θ_2	Final cal. Temp. θ_2	Water 0° to θ_2 (cal$_{15}$)	Ice, −0°.72 to Water 0°	Latent Heat (15° cal.)
1913.												
Feb. 13	66 Plate	409	39160	−255	25	7	55	95.15	15°.12	15.17	79.98	79.61
	67 Plate	428	39964	701	48	8	57	94.92	14°.83	14.88	80.04	79.67
	68 Plate	443	41417	551	26	7	56	94.67	14°.60	14.65	80.02	79.65
	69 Plate	321	34194	−3355	−27	8	55	95.88	15°.79	15.84	80.04	79.67
	70 Plate	369	34597	788	6	7	52	95.67	15°.59	15.64	80.03	79.66
Feb. 14	71 Can	397	38082	−323	22	6	57	94.97	14°.89	14.94	80.03	79.66
	72 Can	453	42363	689	14	7	57	94.96	14°.87	14.92	80.04	79.67
	73 Can	275	25565	620	0	6	50	94.98	14°.96	15.01	79.97	79.60
Feb. 19	79 Can	202	21065	28	11	6	82	103.91	23°.81	23.86	80.05	79.68
Feb. 20	82 Can	213	22111	87	19	5	72	103.75	23°.67	23.72	80.03	79.66
Mar. 29	94 Natrl	536	51072	136	74	10	58	95.59	15°.19	15.24	80.35	reject
	95 Natrl	512	45846	987	27	9	58	91.42	15°.08	15.13	76.29	reject
	96 Natrl	394	37734	−19	−1	9	52	95.60	15°.53	15.58	80.02	79.65
	97 Natrl	398	38071	94	−15	9	55	95.81	15°.76	15.81	80.00	79.63
	98 Natrl	489	45668	1185	28	9	57	95.72	15°.65	15.70	80.02	79.65
												Mean 79.65

TABLE 4

Summary of Experiments by Method of Mixtures (Ice at −0°72)

Date	Sample and source	Mass Ice (grams)	dθ	M×dθ (cal.)	Holder (cal.)	Ice, −0°.72 to water, θ_2	Final cal. Temp. θ_2	Water 0°. to θ_2 (cal$_{15}$)	Ice, −0°.72 to Water, 0°	Latent Heat (15° cal.)
1913										
Feb. 14	74 Can	122	3°.1100	11301	42	92.09	12°.02	12.07	80.02	79.65
	75 Can	129	3°.4470	12509	54	96.56	16°.57	16.62	79.94	79.57
	76 Can	110	2°.9463	10691	52	97.05	17°.02	17.07	79.98	79.61
Feb. 19	77 Can	216	5°.9941	21145	67	97.49	17°.47	17.52	79.97	79.60
	78 Can	205	5°.7323	20218	69	98.20	18°.18	18.23	79.97	79.60
	80 Can	188	5°.2813	18628	60	98.51	18°.43	18.48	80.03	79.66
Feb. 20	81 Can	207	5°.7587	20312	62	97.88	17°.88	17.93	79.95	79.58
	83 Can	190	5°.3010	18698	60	98.21	18°.19	18.24	79.97	79.60
										Mean 79.61

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[37] The material retained in these tables has been selected with two purposes in view: (1) To show the order in which experiments by different methods were carried out, the variation in quantities of ice used, and the values of the principal term and its correction terms; (2) to give complete data necessary to recomputation on the basis of different values for the mechanical equivalent of heat, the specific heat of water and total heat from 0° to various temperatures, and the specific heat of ice.

TABLE 5

Summary of Experiments by Electrical Method (Ice at −3°78)

Date	Sample and source	Mass Ice (grams)	Elect. Energy ÷4.187	$M \times d\theta$ (cal.)	Cooling cor. (cal.)	Stirrer (cal.)	Holder (cal.)	Ice, −3°78 to Water, θ_2	Final cal. Temp. θ_2	Water 0° to θ_2 (cal$_{15}$)	Ice, −3°78 to Water, 0°	Latent Heat (15° cal.)
1913												
Feb. 5	51 Can	546	52993	−94	87	10	67	97.00	15°36	15.41	81.59	H specific heat of ice=0.52.
	53 Can	506	48718	99	47	10	71	96.49	14°81	14.86	81.63	
	54 Can	382	36516	386	41	8	59	96.54	14°88	14.93	81.61	
	55 Can	377	36503	4	39	8	63	96.75	15°09	15.14	81.61	
Feb. 6	56 Can	487	47753	−288	71	10	72	97.50	15°86	15.91	81.59	
	57 Can	491	47311	36	41	10	68	96.45	14°80	14.85	81.60	
	58 Can	315	30189	245	28	7	62	96.47	14°81	14.86	81.61	
	59 Can	470	45590	−173	4	9	65	96.60	14°90	14.95	81.65	
	60 Can	313	30360	−64	12	8	59	96.61	14°93	14.98	81.63	
Feb. 7	61 Can	484	46817	−90	24	10	68	96.46	14°82	14.87	81.59	
	62 Can	482	46237	286	35	11	68	96.43	14°76	14.81	81.62	
	65 Can	365	35224	22	21	9	59	96.35	14°71	14.76	81.59	
										Mean	81.61	
										0.52 × 3.78 =	−1.96	
												79.65

1. Five observations, by the electrical method, on samples of commercial plate ice, give for the heat of fusion 79.65 cal.$_{15}$ per gram mass, with a mean variation of 0.02 calorie.

2. Five observations, by the electrical method, on commercial can ice give 79.65 cal.$_{15}$ per gram mass, with a mean deviation of 0.02 calorie.

3. Eight observations, by the method of mixtures, on commercial can ice give 79.61 cal.$_{15}$ per gram mass, with a mean deviation of 0.02 calorie.

4. Five observations, by the electrical method, on Maine natural ice were made, of which three are consistent with each other and with other results while two (Mar. 29, Nos. 94 and 95) are so discordant and differ so much from other results as to justify their omission. The three determinations give 79.64 cal.$_{15}$ per gram mass, with a mean deviation of 0.01 calorie.

The mean of results by the electrical method is

$$79.65 \text{ cal}_{15}$$

if the ratio of the calorie$_{15}$ to the joule be taken as 4.187.

The mean of results by the method of mixtures is

$$79.61 \text{ cal}_{15}$$

independently of the ratio of the joule to the calorie.

The mean of the 21 observations gives for the heat of fusion of ice

$$79.63 \text{ cal}_{15} \text{ per gram mass}$$

or

$$143.3_8 \text{ Btu}^{28} \text{ per pound mass}$$

or

approximately 143.5 Btu per pound weighed in air against brass or iron weights.

VII. SUMMARY

The work of previous investigations is briefly reviewed and the results tabulated.

The apparatus and procedure of the present investigation are fully described.

Samples of ice prepared in the form of hollow cylinders containing from 100 to 500 grams were cooled to a uniform temperature of either $-0°.72$ or $-3°.78$, weighed while at these temperatures, and introduced into the water of the calorimeter.

Observations were made by two independent methods, one of which, an electrical method, serves to reduce the usual calorimetric corrections to an almost negligible quantity and gives the results primarily in terms of the joule as defined by the electrical units. The second was the method of mixtures which gives the heat of fusion in calories.

The details of computation for observations taken by each method are given in full.

Results.—The heat of fusion of 92 samples of ice from various sources was determined by the two methods.

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[28] The British thermal unit (Btu) is here taken as the quantity of heat required to raise the temperature of a pound mass of water 1° F at 59° F (15° C).

The results of these determinations indicate that for commercial can ice, commercial plate ice, natural ice, ice frozen in the laboratory from air-free double-distilled water and from double-distilled water containing air, all of which were very pure as indicated by electrical conductivity tests, the heat of fusion is the same to within the limits of accuracy of the earlier determinations, i. e., about 1 part in 1000. Further experiments on the three commercial forms of ice fail to show differences greater than about 1 part in 5000.

Five observations on ice contaminated with a mixture of ammonia, sodium chloride, and calcium chloride to the extent of about 1 part in 1000 give results about 1.4 per cent lower than for pure ice.

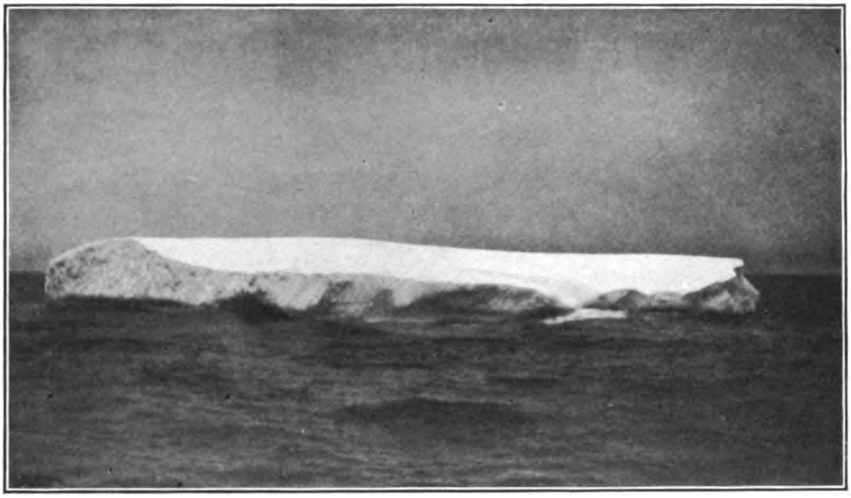
The mean of the final 21 determinations on samples of plate, can, and natural ice gave for the heat of fusion:

$$79.63 \text{ cal}_{15} \text{ per gram mass,}$$

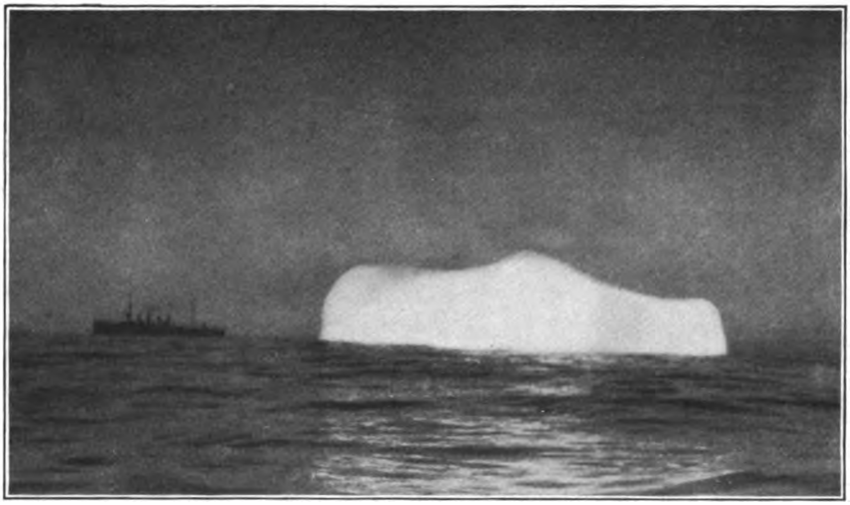
$$\text{or } 143.3_3 \text{ Btu per pound mass,}$$

or 143.5 Btu per pound weighed in air against brass or iron weights.

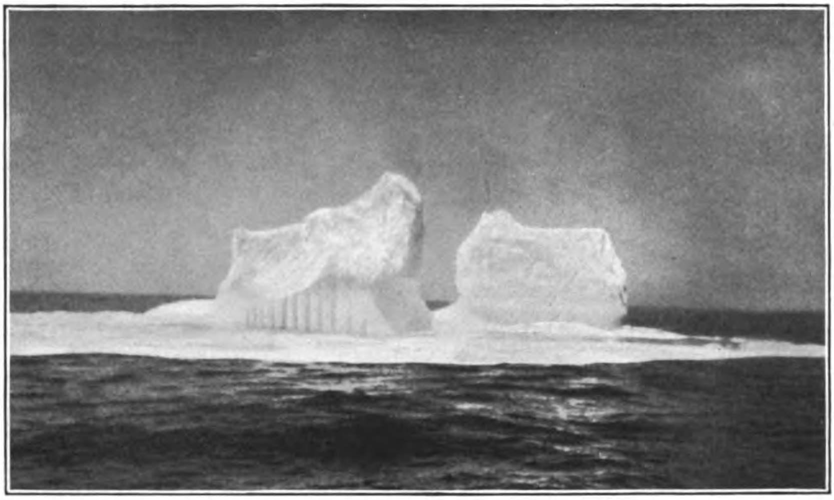
WASHINGTON, August 20, 1913.



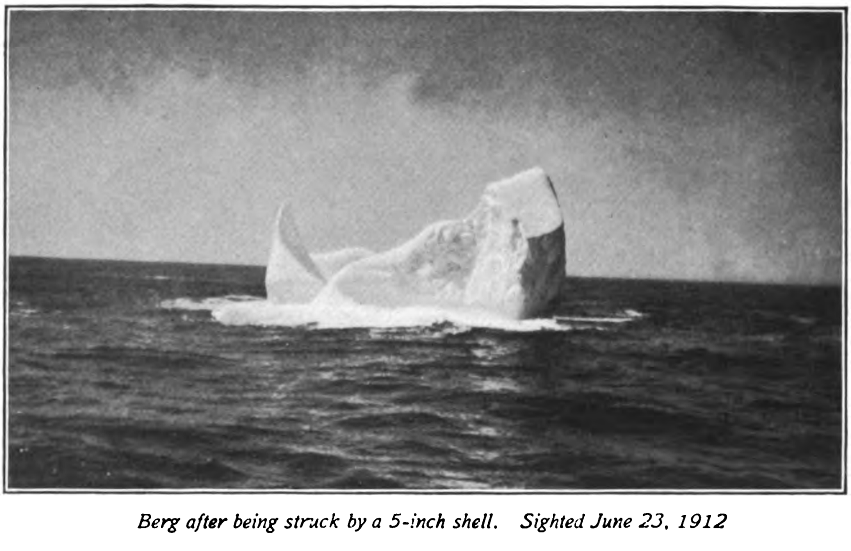
A berg about 40 feet high and 300 feet long. Sighted July 1, 1912



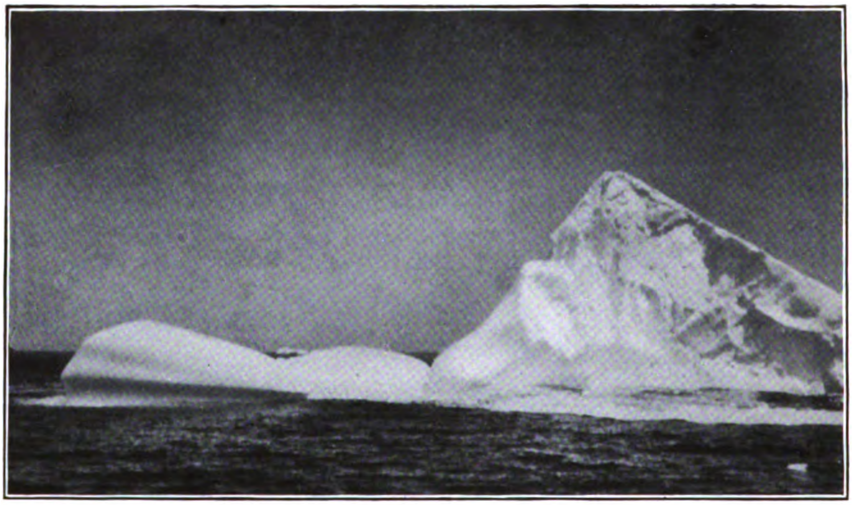
400,000-ton berg with U. S. S. "Chester" in background. Sighted June 17, 1912



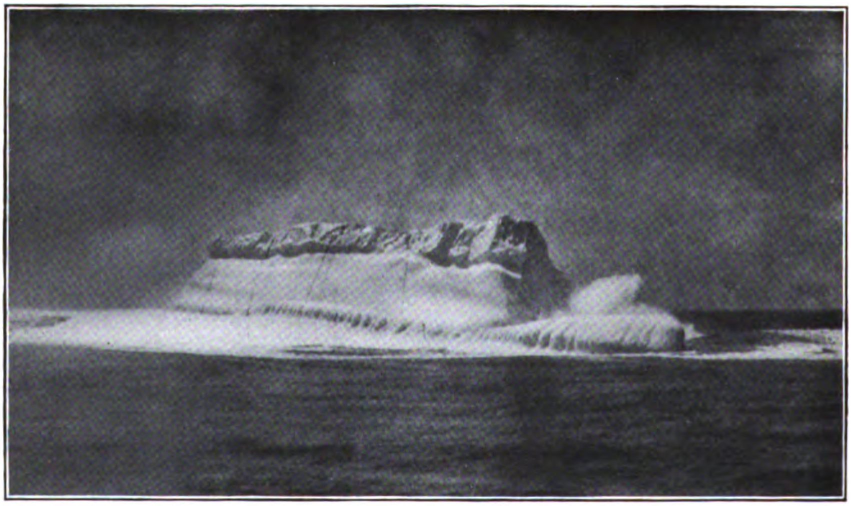
Berg after being struck by three 3-inch shells. Sighted June 23, 1912



Berg after being struck by a 5-inch shell. Sighted June 23, 1912



Berg showing a dangerous projection which has just been brought to the surface by the turning of the berg. Sighted July 2, 1912



Another view of above showing the original water line. Height about 125 feet

OBSERVATIONS ON OCEAN TEMPERATURES IN THE VICINITY OF ICEBERGS AND IN OTHER PARTS OF THE OCEAN

By C. W. Waidner, H. C. Dickinson, and J. J. Crowe

Through the courtesy of the Navy Department an opportunity was afforded to the representatives of the Bureau of Standards to make observations on the temperature of sea water in the vicinity of icebergs and in the open sea with a view to obtaining information on the possibility of detecting the proximity of ice from temperature records. It is fairly evident from a long experience of navigating officers that the usual methods of taking the temperatures of sea water at widely separated intervals of time can give no useful information so far as detecting the proximity of icebergs is concerned. If any variations in the temperature are caused by the presence of ice, then continuous records of the temperature should be taken. The object of these experiments was to obtain such records and then to carefully analyze them with the view to ascertaining whether the proximity of icebergs gives rise to any definite temperature variations which can be distinguished from the accidental variations usually found in sea water.

The Bureau party embarked on the U. S. S. *Chester*, leaving Philadelphia on June 2, 1912, under command of Capt. Decker. Mr. Crowe subsequently transferred to the U. S. S. *Birmingham*, under command of Capt. Hughes, and continued observations from June 19 until the return to the port of Philadelphia on July 11, 1912.

TEMPERATURE EQUIPMENT

The apparatus assembled for these experiments consisted of the following:

One electrical resistance thermometer with 50-foot leads, and one with 150-foot leads, protected and insulated by 4-ply rubber hose, the longer hose being reinforced with wire rope (the thermometers were of the Callendar compensated type with four flexible copper leads and coil of silk-covered nickel wire of about 100 ohms resistance); a surface electrical resistance thermometer, shown in Fig. 1, consisting of a flat coil of silk-covered nickel wire inclosed between copper sheets and insulated by thin layers of mica (the resistance of the nickel coil was about 100 ohms); deep-sea thermometers of the Negretti and Zambra type, kindly loaned by the Bureau of Fisheries; several standard mercurial thermometers; a Leeds & Northrup recorder, Fig. 2, suitable for use with the resistance thermometers, and which was kindly loaned for these experiments by the Leeds & Northrup Co; a Siemens & Halske Wheatstone bridge; a Leeds & Northrup Wheatstone bridge with Kohbrausch slide wire; a Leeds & Northrup marine D'Arsonval galvanometer; a Siemens & Halske high-resistance millivoltmeter; tools, wire, repair parts, etc.

All of the apparatus was carefully calibrated before leaving the laboratory.

The surface thermometer was mounted with its flat face directly against the inner surface of the ship's three-eighths-inch plates, about 6 feet below the water line. The location of the thermometer was in the torpedo room, forward, and on the starboard side. The thermometer was held into good contact with the plate by a suitable wooden strut which was thermally insulated from the thermometer by a layer of felt, and the whole protected by a thick layer of cotton to eliminate the effects of the temperature of the torpedo room. Special experiments showed that this thermometer responded quickly to changes of temperature of the surface with which it was in contact. Simultaneous measurements of temperature made with a sensitive mercurial thermometer in the injection water and with the surface thermometer and recorder, mounted as above, showed that the sudden changes in sea-water

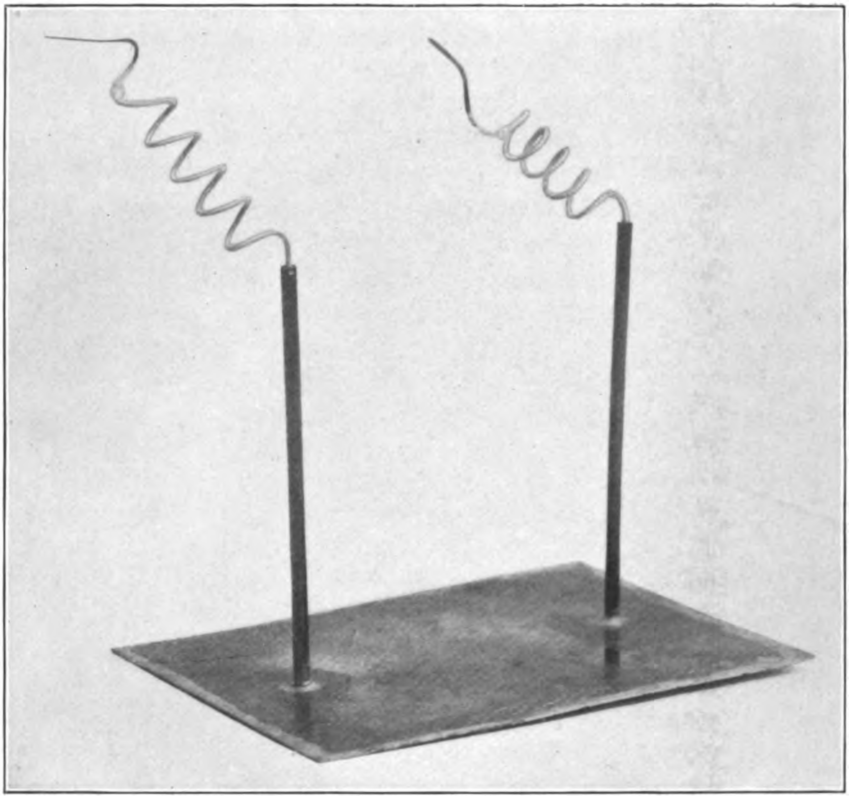


Fig. 1.—*Surface electrical resistance thermometer*

temperature were indicated by the recorder without any significant time lag. As an additional check on the calibration of the surface thermometer it was compared frequently with standard mercurial thermometers.

The recorder was mounted on both ships in the torpedo room near the surface thermometer. The suspended system of the D'Arsonval galvanometer of this recorder was so carefully balanced by the makers that the records were entirely unaffected by the rolling and pitching of the ship, which was by no means inconsiderble, the rolling sometimes amounting to 20° to 30° on each side of the vertical. As used, a change of 1° C corresponded to a movement of the pen of 18 mm on the record sheet. The displacement of the paper was about 60 mm per hour. Full details of the operation of this recorder have been published in the current engineering literature and may be had from the makers. This recorder, with the surface thermometer above described, gave such excellent satisfaction that it was not necessary to use any of the other apparatus which was taken on the trip for emergency use.

TEMPERATURE RECORDS

Practically continuous temperature records were obtained from June 4 until July 10, 1912. The temperatures recorded ranged from 3° to 25° C. The balance point of the recorder was changed to bring the temperature records on the paper by the insertion of suitable known resistances in one arm of the Wheatstone bridge circuit of the recorder, the calibration of the surface thermometer being made with the corresponding resistances in the circuit.

Sample records, together with a brief description of the conditions under which they were obtained, are given in Figs. 3–14.

Fig. 3 shows the temperature record obtained on board the U. S. S. *Chester* June 17, 1912. Several small bergs or growlers were sighted on the horizon at 9.45 a. m. Almost simultaneously the record shows a sudden fall of temperature from 8°.7 to 7°.3 C, or nearly 1°.5 C. At this time the ship was over 10 miles from the nearest of the growlers. The temperature continued to fall irregularly as the growler was approached until 10.45 a. m., when the temperature was 5°.7 C. at which time the distance from the growler, estimated by the range finder, was about 500 yards. At 11 a. m. the distance was about 150 yards. A party put out in a boat to take observations of temperature around the growler. In going around this growler, the mass of which was estimated at about 12 000 tons, the surface temperature as determined by the observers in the lifeboat ranged from 5°.8 to 6°.7 C.

At about 1.20 p. m. the ship got under way, steaming toward a large berg about 12 miles distant. The course of the ship around this berg is shown by the diagram in the upper right corner of Fig. 3. The course D is about 6 or 7 miles in length. The various legs of this course A, B, —G are also indicated on the temperature record, Fig. 3. No significance can be assigned to the irregular fluctuations of temperature observed around this berg. (See Fig. 15.)

About 5.25 p. m. the ship lay to abeam of the berg at a distance of 300 yards. A party put out in a small boat for temperature observations. The time until about 7 p. m. was spent in the immediate neighborhood of the berg, the ship sailing around the berg while the party in the small boat were taking observations. From about 7 to 9.30 p. m. the ship lay to; by this time the ship and berg had drifted apart. During the remaining time, until about midnight, the ship cruised around in an unsuccessful effort to locate the berg with the aid of two powerful searchlights.

From measurements made with two stadimeters, on the ship and on the whaleboat, respectively, the dimensions of the berg were determined. The mass of ice in this berg was thus estimated at about 400 000 tons.

The mean of a number of temperature observations taken from the whaleboat gave the following surface temperatures: 20 feet from the berg, 4°.5; 35 feet, 4°.9; 50 feet, 5°; 75 feet, 5°.4; 200 feet, 5°.7 C. The temperature at a distance of 50 feet from the berg and at a depth of 5 fathoms was 3°.6, and at a depth of 20 fathoms 3°.3. At some miles distant from the berg temperatures were encountered as low as those observed a few feet from the berg.

Although the effort to locate the berg with the aid of searchlights was unsuccessful, at daybreak on the morning of the 18th the berg was in plain view. Between 6 and 7 a. m. the berg turned over in

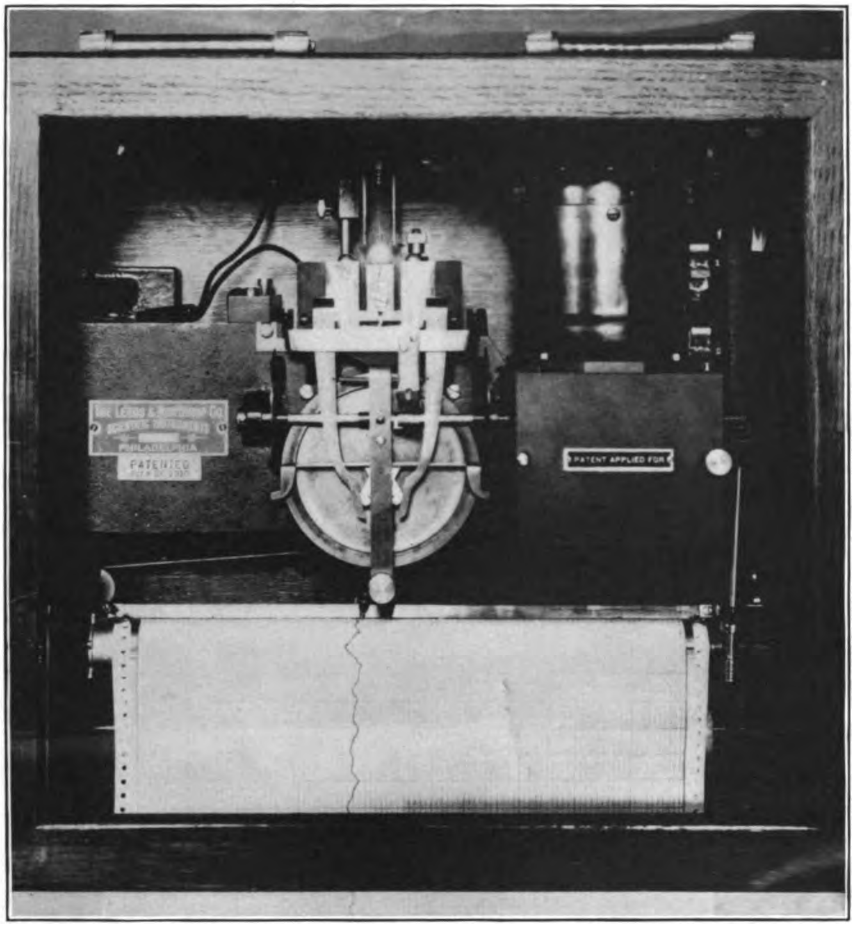

THE LEEDS & NORTHRUP CO.
SCIENTIFIC INSTRUMENTS
PHILADELPHIA
PATENTED
PATENT APPLIED FOR

Fig. 2.—*Leeds & Northrup recorder*

an interval of about 10 minutes, accompanied by several loud reports similar to the reports caused by firing 3-inch guns.

On the morning of June 18 some time was spent in experiments to detect possible echoes, submarine and aerial, which are referred to elsewhere. At 9 a. m. the ship got under way, starting from a point about 2 miles distant from the berg. The ship's course for the day is shown in Fig. 4. Attention is called to the remarkable similarity in the temperature records obtained in going away from and in returning to the morning position of the berg, although the courses traversed are not quite the same. On returning to the approximate position of the berg it was dark and foggy and it could not be again located, even with the aid of searchlights. From the temperature record it would appear that the ship was in the same water at 8 p. m. as it had left at 9 a. m.

Fig. 5 shows the temperature record corresponding to the following log: Ship approached berg steaming at 10 knots, having left a large berg at 12.23 p. m., and was abeam, 200 yards distant, at 2 p. m. About 30 miles distant from this berg the ship passed a large growler, 200 yards distant; time, 5.20 p. m.

The temperature record in approaching and leaving two bergs and a number of growlers and in steaming around one of the bergs is shown in Fig. 6.

Fig. 7 shows the temperature records obtained at night while steaming various courses around growlers in an attempt to locate the position of a large berg that was in plain view at daybreak the next morning. The portion of the curve after 4.30 p. m., when the ship was leaving the ice, is characteristic of temperature changes often observed in the open sea with no ice in sight.

Fig. 8 shows typical variations in sea-water temperatures, similar to those in the latter part of Fig. 5, with no ice in sight. The variations in the temperature here observed are as great and as sudden as any recorded in the neighborhood of bergs.

Fig. 9 shows the temperature record obtained when approaching the Grand Banks of Newfoundland. The drop in temperature here observed is similar to that observed by Barnes[1] in approaching land or shallow water.

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[1] Report on the Influence of Ice Bergs and Land on the Temperature of the Sea, etc., supplement to the Forty-fifth Annual Report of the Department of Marine and Fisheries, 1911-12.

Fig. 10 shows the temperature records for the following log: 9.50 a. m., passed berg 400 yards abeam; 11.35 a. m. to 12 noon, steamed around berg, when ship lay to with berg 75 yards abeam; 1 p. m., ship got under way, berg then 1,100 yards distant; 1.55 p. m., ship headed for another berg sighted five minutes before; 4 p. m., ship lay to in dense fog; 4 to 6 p. m., when fog lifted, three new bergs were in view.

Fig. 11 is the temperature record obtained under conditions which are fully set forth in the figure.

Fig. 12 is the temperature record obtained in approaching, steaming around, and leaving a large berg.

Fig. 13 shows the temperature record obtained on July 6, on the return trip of the U. S. S. *Birmingham* in steaming west along latitude 42° 23′ from longitude 48° 54′ (at 8 a. m.) to 51° 28′ (at 8 p. m.). This curve shows typical variations in ocean temperatures. The variations are large and sudden, although no ice is near.

Fig. 14 is the temperature record in steaming along course latitude 41° 51′, longitude 60° 14′ (at 8 a. m.), to latitude 41° 26′, longitude 63° 07′ (at 8 p. m.).

VARIATIONS IN THE SALINITY OF SEA WATER

Variation in the salinity of sea water in the neighborhood of icebergs due to the diluting action of the water resulting from the melting of the ice is so small as to be entirely masked by the accidental variations found in sea water. The following determinations of the densities of samples of sea water, taken under conditions specified and which were afterwards tested in the laboratories, will serve to illustrate this:

Sample	Specific gravity at $\frac{20^\circ}{4^\circ}$ C	Remarks
1	1.02339.	Close to berg
2	1.02352	Close to another berg
3	1.02340	400 yards from berg
4	1.02336	40 miles from berg
5	1.02319	60 miles from berg
6	0.99923	Water from berg ice
7	0.99923	Distilled water

ECHOES FROM ICEBERGS

The testimony of numerous observers is in evidence that the echo of the foghorn may frequently, but by no means always, be detected when in the proximity of an iceberg or even of a bank of fog. The amount of evidence on this point leaves no doubt as to the correctness of the above statement. The experiment of sounding the foghorn when in the vicinity of a number of the bergs encountered on the trip was tried, but in no instance was an echo detected.

A few experiments were also made to determine whether an echo could be detected under water coming from the larger submerged portion of the berg. For this purpose the ship's bell was lowered into the water and signals produced by striking the bell. Observers stationed at the ship's submarine signal telephones listened for evidences of the echo. The ship was at a distance of 1 to 2 miles from the fair-sized berg encountered by the U. S. S. *Chester* on the afternoon of June 17. It was difficult to draw positive conclusions on account of the disturbing noises present in the telephone receiver, but a number of observers were convinced that they heard faint echoes. There was no time to investigate and improve the telephonic apparatus, so that the most that can be said is that these preliminary experiments looked hopeful enough to merit more careful experiments along these lines.

OTHER OBSERVATIONS

The results of other experiments, such as firing 3 and 5 inch shells into the berg, the utility of searchlights in locating bergs at night, etc., will undoubtedly be covered in the official reports of the commanding officers. It may be worth while to record, in passing, for the information of the reader, the general impressions of the authors, unfamiliar with such matters, that the effects of cannon fire in breaking up icebergs were disappointingly small and the utility of powerful searchlights in their location surprisingly limited.

Although the lookouts were provided with spyglasses or with binoculars, it is of interest to note that the icebergs were invariably first seen with the unaided eye. The difficulty of picking up icebergs under some conditions is illustrated by the following incident: While the ship was steaming toward a large berg in sight a heavy fog fell. There was one lookout in the crow's nest, four on the bridge, and two in the ship's eyes. Notwithstanding this the berg was first picked up from the quarterdeck after the ship had passed some 200 yards abeam.

Samples of ice broken from the berg by gun fire were taken aboard ship. These contained considerable amounts of included air, which probably accounts for their white appearance. The ice was surprisingly hard and free from any definite cleavage planes. The whitish appearance was generally characteristic of all the bergs met with. In some instances there were narrow streaks of ice, transparent and of a blue color, that penetrated entirely through the bergs.

The water resulting from the melting of the berg ice was found to have the same density as that of distilled water. (See p. 8.) It was free from any characteristic taste.

So far as our observations go, the temperature of the air furnishes no evidence of value as to the proximity of a berg.

DISCUSSION OF OBSERVATIONS

An examination of the temperature records herewith submitted, which were obtained under a variety of conditions in the region 37° to 43° 30′ north latitude and 43° to 53° west longitude, at once impresses one with the difficulty of separating the large and sudden variations of sea-water temperature, so frequently met with, from any variations that may be caused by the proximity of icebergs. The authors have obtained records in some parts of the ocean in which the temperatures were practically constant to a few tenths of a degree for many hours. On the other hand, some of the sample records submitted show that the temperature variations in other parts of the ocean, where no ice is near, are as great and as sudden as any observed in the neighborhood of bergs. Having established the existence of such variations in sea-water temperatures, it follows that it will be very difficult and often impossible to draw definite conclusions as to the proximity of ice from temperature records.

In approaching or leaving a berg the temperature of the sea water may rise or fall or remain practically constant. Thus in Fig. 3, in approaching the large berg along course D, the temperature varied irregularly through a range of about 0.2° C, a variation much less than is frequently observed in this distance. Along some of the courses the temperature fell in approaching the berg (e. g., course A), and along course G, for example, the temperature varied quite irregularly. In Fig. 15 the temperature records of Fig. 3 are reproduced, the temperature at the iceberg being arbitrarily taken as the zero of temperatures for each course. Curve *a*, Fig. 15, is the temperature record in approaching and leaving a growler. The remainder of the curves in this figure (15) are the records for all the courses around the large berg, shown in Fig. 3. The temperature records for the different courses differ so much that no certain effect can be attributed to the iceberg. The mean of the curves for all the courses is shown in the lower part of Fig. 15.

In Fig. 16 are reproduced all the temperature records given, except those of June 17, for approaching and leaving icebergs, the temperatures at the bergs being always arbitrarily taken as the zero of temperature. The mean curve shown below indicates that in general there was a fall in temperature of about 1° in 4 or 5 miles in approaching the various bergs. In all but two instances the minimum temperature was found near the bergs.

The temperature records published by Prof. Barnes very generally show a rise in temperature as a berg is approached, occasionally accompanied by a slight fall in temperature very near the berg. Prof. Barnes regards the rise of temperature as the "characteristic iceberg effect" and attributes any drop in temperature to cold currents. His records show the normal variations of sea-water temperature in the localities of his observations to be very much smaller than were observed in the parts of the ocean where our observations were made. Although many of the small temperature variations which appear significant in his records would be completely masked by the large and sudden temperature changes which our records show, nevertheless the magnitude of the so-called "iceberg effect" observed by Prof. Barnes being often 0 5° to 2° C, such changes would be very evident on our records where changes of a few hundredths of a degree are readily discernible.

Our records do not corroborate Barnes's characteristic iceberg effect. Twelve of the 14 curves, as well as the mean curve, of Fig. 16 certainly show no such rise in temperature. Most of these curves indicate the opposite effect.

As Prof. Barnes's and our own records are matters of observation which unquestionably represent conditions that were actually encountered, it would seem that the effects due to bergs, if such effects can yet be regarded as established, must be different under different conditions. Indeed, that such is the case is shown by the different temperature records obtained in approaching a given berg along different courses.

Enough data is not yet at hand to formulate a theory to account for the variations of temperature observed in the vicinity of icebergs. Indeed, the question is still in doubt as to whether they influence to any measurable extent the temperatures of sea water at any considerable distance (a mile or so).

In view of the observations of Barnes and of the authors on the salinity of surface water at different distances from bergs, it seems fairly certain that the layer of cold fresh water resulting from the melting of the berg, and which was supposed on Pettersson's theory to spread out over the surface in the vicinity of an iceberg, causes no measurable dilution or change of salinity of the surface layer.

Barnes's records so uniformly show a rise of temperature as the berg is approached that he has termed this observed rise "the iceberg effect." This effect is not characteristic of our records. Indeed, on the average, the authors observed a fall in temperature from a distance of several miles up to the bergs. In view of the erratic variations of the temperature of these parts of the ocean when no ice is near and of the fact that in approaching a given berg along different courses the temperature variations are quite different (being nearly constant over some courses and falling very appreciably over other courses), we would not deem it justifiable to conclude that the observed variations were certainly connected with the presence of the bergs.

It is interesting to inquire a little further into the question whether any cooling action of the berg could be expected to make itself felt at any considerable distance from the berg. If the berg is constantly drifting into new waters, such effect would obviously be impossible from the consideration of the fact that it would require the melting of about a million tons of ice to cool 1 square mile of the ocean to a depth of only 25 feet by 1° C.; hence the possibility of any significant cooling action would require that the berg and the water in which it is immersed drift together for a considerable period of time, i. e., that the relative motion be small. This is probably true under some conditions, but by no means always. Considerations, such as these, of the enormous mass of ice required to produce a cooling action distinguishable from temperature variations due to other causes, the slowness of melting of the berg, etc., render it doubtful whether any such effect could be distinguished with certainty at distances of a mile or so. To account for the observed rise in temperature or "iceberg effect" Barnes has advanced an ingenious theory. He assumes that in regions of the ocean at some distance from the berg the surface layer, heated by solar radiation, is mixed with the colder water below by the "normal vertical circulation," while near the berg there is a current set up toward the berg due to the combined effects of the melting and cooling action of the berg. This current toward the berg, it is assumed, interferes with the "normal vertical circulation" so that the warm water remains on the surface. It is difficult to understand how a sufficiently strong current toward the berg could be set up by the melting and cooling action of the berg to interfere with the "normal vertical circulation" at a distance of a mile or two. That there is no very strong current toward the berg seems to be indicated by the drifting apart of the fragments of a berg from the berg itself or of the larger parts of a berg after breaking up. Difference of wind action may, however, complicate any conclusions based on such observations.

CONCLUSIONS

The records of sea-water temperatures obtained by means of an electrical resistance thermometer and a Leeds & Northrup temperature recorder, installed on the U. S. S. *Chester* and *Birmingham* in their patrol of the North Atlantic Ocean in June and

July, 1912, show that the temperature variations in parts of the ocean far removed from ice are often as great and sudden as in the neighborhood of icebergs.

For a majority of the courses of the ship in the vicinity of icebergs there was a fall in temperature from a fraction of a degree to 3° in a distance of 4 or 5 miles on approaching the berg. Records were obtained, however, in which the character of the temperature variation varied with the direction of approach to the berg, the temperature being nearly constant over one course, while over other courses the temperature rose or fell as the berg was approached. So far as our records go, therefore, it does not seem possible to draw positive conclusions as to the absence or proximity of ice from the temperature records of sea water. This is not a condemnation of the use of suitable recorders on ships. As Barnes has shown, the temperature record may give valuable information on the approach to shore and shallow water, on the identification of characteristic ocean currents, and, as his records seem to show, even of the proximity of icebergs in some parts of the ocean where the variations are less erratic than in the regions in which our observations were made.

If the "characteristic iceberg effect" observed by Barnes, i. e., rise of temperature on approaching icebergs, had been present around the bergs observed by us and of the same or even much less magnitude, our records would have rendered such an effect evident, notwithstanding the irregular variations of temperature usually found to exist. In view of the differences in the character of the records obtained by Barnes and ourselves, it is very desirable that further observations be made in different parts of the ocean, and under as varied conditions as possible, before attempting to draw final conclusions.

In conclusion the authors wish to express their deep sense of obligation to Capt. Decker and Capt. Hughes and to their officers and crews for hearty cooperation and many acts of kindness during their stay on shipboard.

WASHINGTON, August 1, 1913.

3

3
1°C =18 MM
1 HOUR =ABOUT 60
2

42°49′ N.
49°08′ W.
STEAMED AROUND BERG
LAY TO BERG 75 YDS.
BERG 1100 YDS.
12 O'CLOCK M.
1 O'
RED VARIOUS CO
11

FIG. 1

57′
P21′

ACTU
CK M

12

FIG.

ACCURACY OF THE FORMULAS FOR THE RATIO, REGULATION, AND PHASE ANGLE OF TRANSFORMERS

By P. G. Agnew and F. B. Silsbee

There has been a great deal of discussion of the formulas for the predetermination of the performance of transformers from the constants obtained from the "short circuit" and "open circuit" tests, particularly in regard to the formula for computing regulation. We have very little data available, however, which will enable one to compare the formulas with accurately observed values. Bedell [1] and Drysdale [2] have published results for some of the formulas, which show a very fair agreement but so far as the authors are aware no comparisons have hitherto been published based on the precise potentiometer methods now available for the direct determination of ratio, regulation, and phase angle.

DERIVATION OF FORMULAS

The derivation of these formulas is given below in rather extended form in order to show the magnitude of the approximations which are introduced. These approximations will be considered in greater detail than might seem necessary, but on account of the confusion which has arisen from the use of incorrect formulas for regulation, some of the larger central stations have requested such a detailed discussion. A derivation of the formula for regulation has been published by one of the authors in conjunction with Dr. M. G. Lloyd.[3] As this formula may be developed with only a slight amount of extra work while deriving those for ratio and phase angle, its derivation is given here in a slightly more rigorous form.

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[1] Bedell, Chandler, and Sherwood: Elect. World, **30**, p. 190; Aug. 14, 1897.

[2] Drysdale: Electrician, **65**, p. 643; July, 1910.

[3] Lloyd and Agnew: This Bulletin, **6**, No. 2, p. 273; 1909. Reprint No. 129.

Let N = ratio of turns, primary to secondary.

E_1, E_2, E' = primary and reversed secondary terminal voltages, and primary induced voltage, respectively.

R_1, X_1, Z_1 = primary resistance, reactance and impedance.

R_2, X_2, Z_2 = secondary resistance, reactance and impedance.

R, X, Z = total resistance, reactance and impedance, referred to the primary, so that

$$R = R_1 + N^2R_2, \quad X = X_1 + N^2X_2, \quad Z = Z_1 + N^2Z_2$$

$I = \frac{I_2}{N}$ = load current referred to primary side.

θ = angle by which I lags behind E_2.

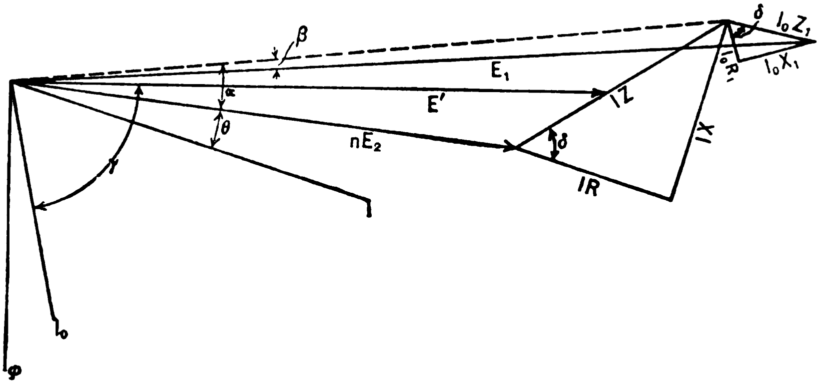

Fig. 1.—*Vector diagram of transformer voltages*

$I_0, I_0 - \Delta I_0$ = exciting current at no load and at full load, respectively.

φ = flux.

$\gamma, \gamma + \Delta\gamma$ = angle by which the exciting current lags behind the induced voltage at no load and at full load, respectively.

α = part of phase displacement caused by load current.

β = part of phase displacement caused by exciting current.

$$\delta = \tan^{-1}\frac{X}{R}$$

Then in Fig. 1 the vector difference between E_1 and NE_2 is made up of four parts, IR and IX in phase and in quadrature, respectively, with I, and I_0R_1 and I_0X_1 in phase and in quadrature, respectively, with I_0.

It is necessary to assume $X_1 = N^2X_2$, since the reactances of the individual windings can not be directly determined independently. We shall assume $\frac{X_1}{R_1} = \frac{X_2}{R_2} = \frac{X}{R}$, but only in those terms which contain the exciting current, and as will appear later these whole terms are so small as to be negligible in most practical work.

In fact, it may be shown without trouble that if the whole analysis is carried through, assuming that X_1 and N^2X_2 have any given ratio, and carrying all approximations to the same order as is done in what follows, that the final formulas will not be affected in any way. We may then take E′ as terminating at the midpoint of IZ, and practically bisecting α.

Expressing all vectors in the usual complex notation, and using dotted capitals to indicate complex quantities, we see from Fig. 1

$$\dot{E}_1 = E_1[\cos(\alpha-\beta) + j\sin(\alpha-\beta)]$$

$$\dot{E}_2 = E_2$$

$$\dot{I} = I[\cos\theta - j\sin\theta]$$

and also

$$\dot{Z} = Z[\cos\delta + j\sin\delta] = R + jX$$

At no load we have

$$\dot{I}_0 = I_0[\cos\gamma - j\sin\gamma]$$

and with load

$$\dot{\overline{I_0 - \Delta I_0}} = (I_0 - \Delta I_0)\left[\cos\left(\gamma + \Delta\gamma - \frac{\alpha}{2}\right) - j\sin\left(\gamma + \Delta\gamma - \frac{\alpha}{2}\right)\right]$$

Then we have as our fundamental relation

$$N\dot{E}_2 + \dot{I}\dot{Z} + \dot{\overline{(I_0 - \Delta I_0)}}\,\dot{Z}_1 - \dot{E}_1 = 0$$

$$\therefore\ NE_2 + IZ\{\cos\theta - j\sin\theta\}\{\cos\delta + j\sin\delta\}$$

$$+ (I_0 - \Delta I_0)Z_1\left\{\cos\left(\gamma + \Delta\gamma - \frac{\alpha}{2}\right) - j\sin\left(\gamma + \Delta\gamma - \frac{\alpha}{2}\right)\right\}\{\cos\delta + j\sin\delta\}$$

$$- E_1\{\cos(\alpha-\beta) + j\sin(\alpha-\beta)\} = 0$$

or

$$NE_2 + IZ\{\cos(\theta-\delta) - j\sin(\theta-\delta)\}$$
$$+ (I_0 - \Delta I_0)Z_1\left\{\cos\left(\gamma+\Delta\gamma-\frac{\alpha}{2}-\delta\right) - j\sin\left(\gamma+\Delta\gamma-\frac{\alpha}{2}-\delta\right)\right\}$$
$$-E_1\{\cos(\alpha-\beta) + j\sin(\alpha-\beta)\} = 0$$

Separating real and imaginary parts

$$NE_2 + IZ\cos(\theta-\delta) + (I_0-\Delta I_0)Z_1\cos\left(\gamma+\Delta\gamma-\frac{\alpha}{2}-\delta\right)$$
$$-E_1\cos(\alpha-\beta) = 0 \qquad (1)$$

$$IZ\sin(\theta-\delta) + (I_0-\Delta I_0)Z_1\sin\left(\gamma+\Delta\gamma-\frac{\alpha}{2}-\delta\right)$$
$$+E_1\sin(\alpha-\beta) = 0 \qquad (2)$$

In order to put these equations into usable form, further approximations must be made. In estimating the magnitude of these we may consider two cases:

Case 1.—When the impedance drop is 4 per cent of rated voltage and the magnetizing current is 10 per cent of rated load current. This is a more unfavorable condition than is ordinarily found in practice. Here $\frac{IZ}{NE_2} = 0.04$ and $\frac{I_0Z_1}{NE_2} = 0.002$

Case 2.—When the impedance drop is 2.5 per cent of rated voltage and the exciting current is 6 per cent of rated current. This would cover the great majority of practical cases. Here

$$\frac{IZ}{NE_2} = 0.025 \text{ and } \frac{I_0Z_1}{NE_2} = 0.00075$$

In evaluating the approximations, sines and cosines of the various angles will be taken as unity, in order that the values found may be limiting ones, even under the most unfavorable conditions.

Consider first the magnitude of the term

$$(I_0-\Delta I_0)Z_1\cos\left(\gamma+\Delta\gamma-\frac{\alpha}{2}-\delta\right)$$

in comparison with E_1. Neglecting for the moment ΔI_0 and $\Delta\gamma$, the term can not exceed 0.2 per cent of E_1 for Case 1 or 0.08 per cent for Case 2. The actual values of ΔI_0 and $\Delta\gamma$ require a determination of the rate of variation of I_0 and γ with E_1, measurements which are not ordinarily made. In Case 1 ΔI_0, the change in exciting current from full load to no load, would probably not be greater than 10 per cent of I_0, so that the part of the term depending on ΔI_0 would not exceed 0.02 per cent. For Case 2 the corresponding values would be 6 per cent and 0.005 per cent; that is, it is less than the errors of commercial measurement. A numerical analysis leads to the same conclusion in regard to the effect of $\Delta\gamma$ in both equations 1 and 2.

Hence both ΔI_0 and $\Delta\gamma$ may be neglected and the formulas take the form

$$NE_2 + IZ\cos(\theta-\delta) + I_0Z_1\cos\left(\gamma-\frac{\alpha}{2}-\delta\right) - E_1\cos(\alpha-\beta) = 0 \quad (3)$$

$$IZ\sin(\theta-\delta) + I_0Z_1\sin\left(\gamma-\frac{\alpha}{2}-\delta\right) + E_1\sin(\alpha-\beta) = 0 \quad (4)$$

For no load

$$NE_{2,0} + I_0Z_1\cos(\gamma-\delta) - E_1\cos\beta = 0 \quad (5)$$

$$I_0Z_1\sin(\gamma-\delta) - E_1\sin\beta = 0 \quad (6)$$

From (3)

$$\text{Ratio} = \frac{E_1}{E_2} = \frac{N}{\cos(\alpha-\beta)}\left\{1 + \frac{IZ\cos(\theta-\delta)}{NE_2} + I_0Z_1\cos\frac{\left(\gamma-\frac{\alpha}{2}-\delta\right)}{NE_2}\right\} \quad (7)$$

From (4) and (6) we have approximately

$$\alpha-\beta = \sin(\alpha-\beta) = \frac{1}{E_1}\left[-IZ\sin(\theta-\delta) - I_0Z_1\sin\left(\gamma-\frac{\alpha}{2}-\delta\right)\right] \quad (8)$$

$$\beta = \sin\beta \qquad = \frac{1}{E_1}I_0Z_1\sin(\gamma-\delta) \quad (9)$$

Adding (8) and (9) and neglecting a term of the form $I_0Z_1\cos(\gamma-\delta)\sin\frac{\alpha}{2}$ which in Case 1 could not exceed 0.004 per cent or 0.08 minute, we have

$$\alpha = -\frac{1}{E_1}IZ\sin(\theta-\delta) \quad (10)$$

Expanding the term cos $(\alpha-\beta)$ in (7) and neglecting squares of β and cubes of α (since these are of the order 0.0004 per cent and 0.0003 per cent) and again neglecting the term $\frac{\alpha}{2}$ in the last term of (7) since this is equivalent to the approximation just justified in (10) we have

$$\frac{E_1}{E_2}=N\left\{1+\frac{(\alpha-\beta)^2}{2}+\frac{IZ\cos(\theta-\delta)}{NE_2}+\frac{I_0Z_1\cos(\gamma-\delta)}{NE_2}\right\}$$

or, by (8), retaining only squares of α

$$\frac{E_1}{E_2}=N\left\{1+\frac{IZ\cos(\theta-\delta)}{NE_2}+\frac{I^2Z^2\sin^2(\theta-\delta)}{2E_1^2}+\frac{I_0Z_1\cos(\gamma-\delta)}{NE_2}\right\}\quad(11)$$

For regulation we have from (3) and (5)

$$\begin{aligned}N(E_{2,0}-E_2)&=IZ\cos(\theta-\delta)+I_0Z_1\left\{\cos\left(\gamma-\frac{\alpha}{2}-\delta\right)-\cos(\gamma-\delta)\right\}\\&\quad-E_1\{\cos(\alpha-\beta)-\cos\beta\}\\&=IZ\cos(\theta-\delta)+2I_0Z_1\sin\left(\gamma-\frac{\alpha}{4}-\delta\right)\sin\frac{\alpha}{4}\\&\quad+2E_1\sin\frac{(\alpha-2\beta)}{2}\sin\frac{\alpha}{2}\end{aligned}$$

$$\begin{aligned}\text{Regulation}&=\frac{E_{2,0}-\mathrm{E}_2}{\mathrm{E}_2}\\&=\frac{1}{NE_2}\Bigg[IZ\cos(\theta-\delta)+2I_0Z_1\sin\left(\gamma-\frac{\alpha}{4}-\delta\right)\left(\frac{\alpha}{4}-\frac{\alpha^3}{384}-\right)\\&\quad+2E_1\left\{\frac{\alpha-2\beta}{2}-\frac{(\alpha-2\beta)^3}{48}-\right\}\left\{\frac{\alpha}{2}-\frac{\alpha^3}{48}-\right\}\Bigg]\end{aligned}\quad(12)$$

It will finally appear that the first term in the brackets gives the regulation to 0.1 per cent and all other terms but one are negligible. Hence, as already shown for ratio, we may neglect squares of β, cubes of α, the small angle $\frac{\alpha}{4}$ in the expression $I_0Z_1\sin\left(\gamma-\frac{\alpha}{4}-\delta\right)$, and put NE_2 equal to E_1 in the latter terms, without the error exceeding 0.01 per cent. Substituting values of α and β from (8), (9), and (10) in (12) and making these approximations we have,

$$\text{Regulation} = \frac{IZ\cos(\theta-\delta)}{NE_2} + \frac{I^2Z^2\sin^2(\theta-\delta)}{2N^2E_2^2} + \frac{IZI_0Z_1\sin(\gamma-\delta)\sin(\theta-\delta)}{2N^2E_2^2} \tag{13}$$

In Case 1 the last term is only 0.004 per cent, and so this also may be omitted.

SUMMARY OF FORMULAS

For convenience of reference the formulas for ratio, regulation, and phase angle are here grouped together for various conditions of loading. They are obtained from equations (11), (13), and (8) by means of the relations

$$X = Z\sin\delta \text{ and } R = Z\cos\delta$$

In the derivation, to avoid confusion α was taken positive when the phase relations were as shown in figure 1. In the final formulas given below, however, the sign has been changed so that the phase angle is positive when the reversed secondary voltage leads the primary. When ± signs occur the upper sign should be used for lagging and the lower for leading secondary current.

$$\text{Ratio} = N\left[1 + \frac{IR\cos\theta \pm IX\sin\theta}{NE_2} + \frac{(IR\sin\theta \mp IX\cos\theta)^2}{2N^2E_2^2} + \frac{I_0R_1\cos\gamma + I_0X_1\sin\gamma}{NE_2}\right]$$

$$\begin{matrix}\text{Ratio}\\ (\text{P.F.}=1)\end{matrix} = N\left[1 + \frac{IR}{NE_2} + \frac{I^2X^2}{2N^2E_2^2} + \frac{I_0R_1\cos\gamma + I_0X_1\sin\gamma}{NE_2}\right]$$

$$\begin{matrix}\text{Ratio}\\ (\text{no load})\end{matrix} = N\left[1 + \frac{I_0R_1\cos\gamma + I_0X_1\sin\gamma}{NE_2}\right]$$

$$\text{Per cent regulation} = 100\left[\frac{IR\cos\theta \pm IX\sin\theta}{NE_2} + \frac{(IR\sin\theta \mp IX\cos\theta)^2}{2N^2E_2^2}\right]$$

$$\begin{matrix}\text{Per cent regulation}\\ (\text{P. F.}=1)\end{matrix} = 100\left[\frac{IR}{NE_2} + \frac{I^2X^2}{2N^2E_2^2}\right]$$

$$\text{Phase angle} = \frac{1}{E_1}[IR \sin \theta - IX \cos \theta + I_oR_1 \sin \gamma - I_oX_1 \cos \gamma]$$

$$\begin{matrix}\text{Phase angle} \\ (\text{P. F.} = 1)\end{matrix} = \frac{1}{E_1}[-IX + I_oR_1 \sin \gamma - I_oX_1 \cos \gamma]$$

$$\begin{matrix}\text{Phase angle} \\ (\text{no load})\end{matrix} = \frac{1}{E_1}[I_oR_1 \sin \gamma - I_oX_1 \cos \gamma]$$

(These last three equations give the phase angle in radians. To get minutes, multiply by 3438.)

For most practical work the square terms in the formulas for ratio and regulation may well be omitted.

DISCUSSION OF FORMULAS

The combined approximations made in the deduction of these formulas are less than 0.01 per cent in ratio and regulation, or 0.4 minute in phase angle in Case 2. For Case 1 the approximations may under some conditions add up to 0.03 or 0.04 per cent in ratio and regulation or 1.5 minutes in phase angle. In nearly all practical cases the inaccuracy of the temperature measurements alone is sufficient to cause an error as great as the combined approximations, to say nothing of instrumental errors and the assumption that the reactance under working conditions is the same as that under short circuit conditions.

It is evident from the form of the equations that when plotted against current at a given power factor and voltage the phase angle of a transformer gives a straight line. The ratio and regulation give nearly a straight line, the very slight curvature being due to the square term. With constant secondary current, the phase angle gives a sine curve when plotted against the phase angle of the connected load, crossing the axis of zero phase near the point where $\theta = \tan^{-1}\frac{X}{R}$. Similarly, the ratio and regulation give nearly sine curves (distorted by the square term) which have their maxima where $\theta = \tan^{-1}\frac{X}{R}$. These relations may be found useful even when the short-circuit data are not available.

A question has been raised in regard to the exact definition of rated current and rated voltage of a transformer when the voltage drop within the windings is taken into consideration. It appears that different engineers give different interpretations of the Standardization Rules of the American Institute of Electrical Engineers covering the point, viz: Rules 65, 65a, 67, 68, 69, 70, and 197. Three interpretations may be given, as may be most clearly seen by a particular case, say a 5 kva, 2200/110 volt transformer.

First. Hold 2200 volts on the primary. Draw 5000/110 amperes. Take the reading of a voltmeter placed on the secondary as E_2.

Second. Hold 2200 volts on the primary. Draw 5000 volt amperes from the secondary. Take the readings of voltmeter and ammeter placed in the secondary as E_2 and I_2.

Third. Apply whatever primary voltage is necessary to make $E_2 = 110$ when 5000 volt-amperes are being drawn.

Since the ratio given on the name plate of power transformers is the ratio of turns and not of full-load terminal voltages, these interpretations give slightly different values. While the magnitude involved is small, it is a matter on which the Institute Rules should be definite, since it affects all the factors involved in the rating of transformers. It is to be hoped that the ambiguity will be removed in the next revision.

The third interpretation would seem to be preferable, since rule 65, while applying primarily to power, seems, at least by implication, to indicate that rated voltage is the secondary terminal voltage at rated secondary kva load. We find that this is the interpretation of a number of engineers.

EXPERIMENTAL TESTS OF THE FORMULAS

As a test of the formulas accurate measurements were made of ratio and phase angle of two different types of lighting transformers by the potentiometer method[4] and covering the whole range of power factors from zero power-factor current leading to zero power-factor current lagging.

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[4] For a description of this method, see Agnew and Silsbee, Proceedings A. I. E. E., 31, 1267; June, 1912.

These phase relations were obtained by opposing two similar transformers as in the usual connections for a heat run. The emf which was inserted to circulate the load current was derived from the secondary of a phase shifting transformer excited from a second generator on the same shaft as that which excited the transformer under test. The magnitude of the current could be controlled by the generator field and its phase adjusted independently by the position of the rotor of the phase-shifting transformer. The temperature was maintained very nearly constant during the measurements, and the results have been corrected for the slight variations which did occur. As the transformers were small, it was necessary to correct for losses in the measuring instruments employed.

The impedances were determined by the usual short-circuit test using carefully calibrated portable instruments. In both transformers the resistance was found to be the same on a. c. as on d. c. and the leakage reactance appeared independent of the current up to double-rated current.

Data on Transformers

	Transformer A	Transformer B		Transformer A	Transformer B
Rated kva..................	0.6	5.0	P. F. of exciting current at rated voltage....per cent..	0.39	0.23
Frequency..................	60.0	60.0			
Voltage....................	240/120	1100/110	Increase of voltage to give 11 per cent exciting current ....per cent..	....	23.0
Method of cooling...........	Air only	Oil			
Resistance drop...per cent..	2.3	2.0			
Reactance drop.......do....	1.6	1.0	P. F. at 11 per cent exciting current....................	....	0.09
Impedance drop.......do....	2.8	2.2			
Exciting current at rated voltage..........per cent..	11.0	3.4			

Figs. 2 to 5 have been plotted to show the results of the comparison. Ratio, regulation, and phase angle are plotted against the angle between secondary current and voltage. (Power factors have also been indicated on the axis of abscissas.) The full lines are computed by the formulas from the short-circuit data, while the circles represent observed points. It will be seen that the agreement is quite satisfactory. In the runs plotted

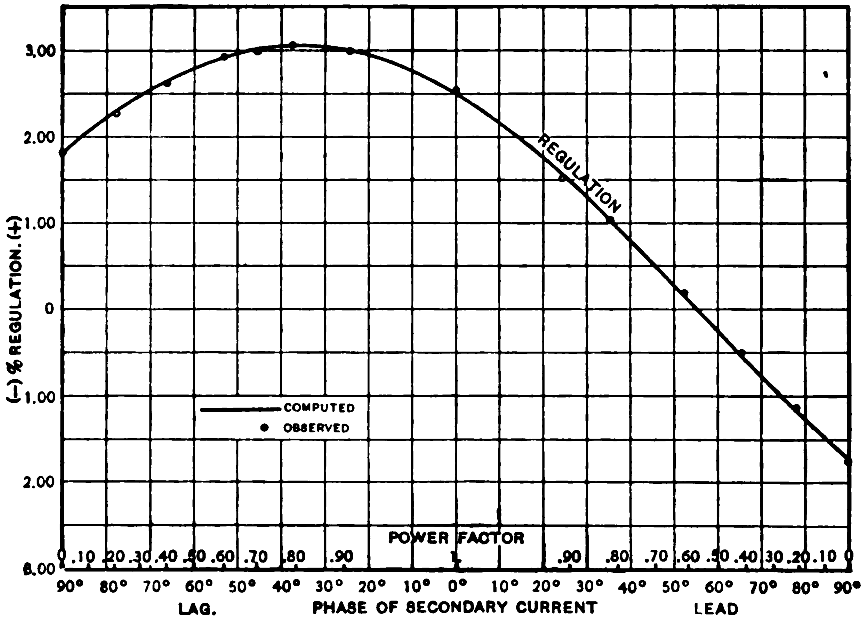

Fig. 2.—*Regulation of a 0.6 kva. 240/120 volt transformer*

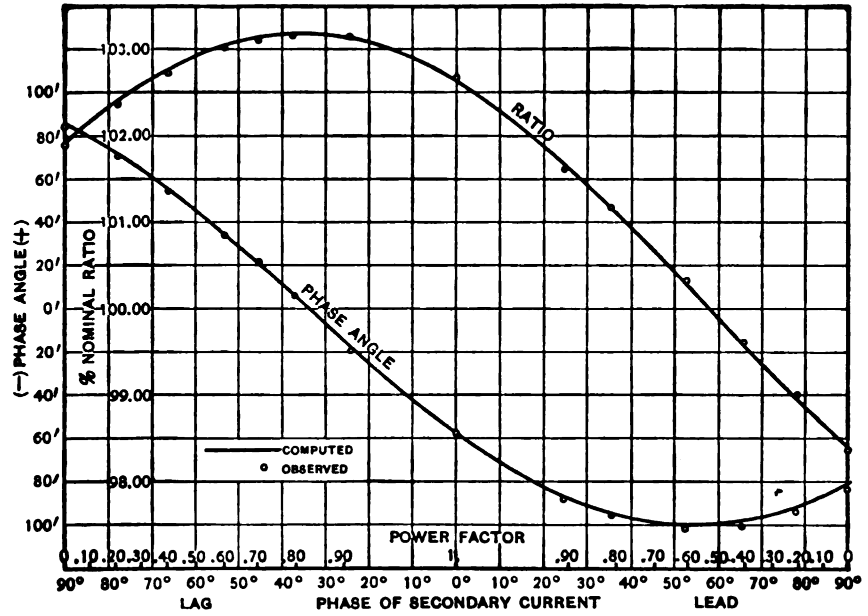

Fig. 3.—*Ratio and phase angle of a 0.6 kva. 240/120 volt transformer*

in Figs. 6 and 7 the voltage on transformer B was arbitrarily raised to give an exciting current of 11 per cent of rated load current, so as to magnify the effect of the approximations made in the derivation of the formulas. The agreement between computed and observed values is entirely satisfactory, again showing that the effect of the exciting current upon the regulation is inappreciable.[5] The current rating was taken as unchanged and hence the regulation is proportionately less than at rated voltage.

The average differences (taken without regard to sign) between the computed and observed values for the various groups of readings are given in the accompanying table. (Since they are averages they are carried to one place farther than the sensitivity of the method of direct measurement.) The average differences taken with regard to sign were negligible, showing that there were no appreciable systematic errors.

Average Difference between Observed and Computed Values.

	Transformer A	Transformer B		Transformer A	Transformer B
Ratio, rated voltage, no load, per cent	0.006	0.010	Regulation, excess voltage, full load ... per cent		0.010
Ratio, rated voltage, full load, per cent	.021	.022	Phase angle, rated voltage, no load ... minutes	0.9	.1
Ratio, excess voltage, no load, per cent		.005	Phase angle, rated voltage, full load ... minutes	1.3	.8
Ratio, excess voltage, full load, per cent		.010	Phase angle, excess voltage, no load ... minutes		.1
Regulation, rated voltage, full load ... per cent	.016	.015	Phase angle, excess voltage, full load ... minutes		1.6

As would be expected, the agreement at no load is better than with load. It should be remembered that the no-load phase angle is computed on the assumption that the reactance drop of the primary is equal to that of the secondary.

It is evident, at least for the two types of transformers represented in these tests, that the short-circuit test gives results which are entirely adequate for the predetermination of the

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[5] For further experimental evidence on this point, see Lloyd and Agnew, this Bulletin, 6, p. 273. Reprint No. 129.

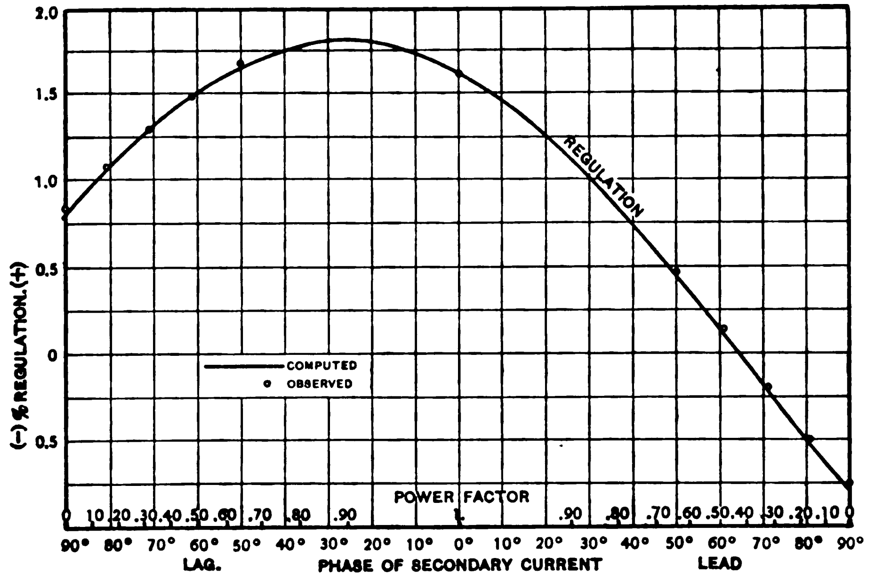

Fig. 4.—*Regulation of a 5 kva. 1100/110 volt transformer at normal voltage*

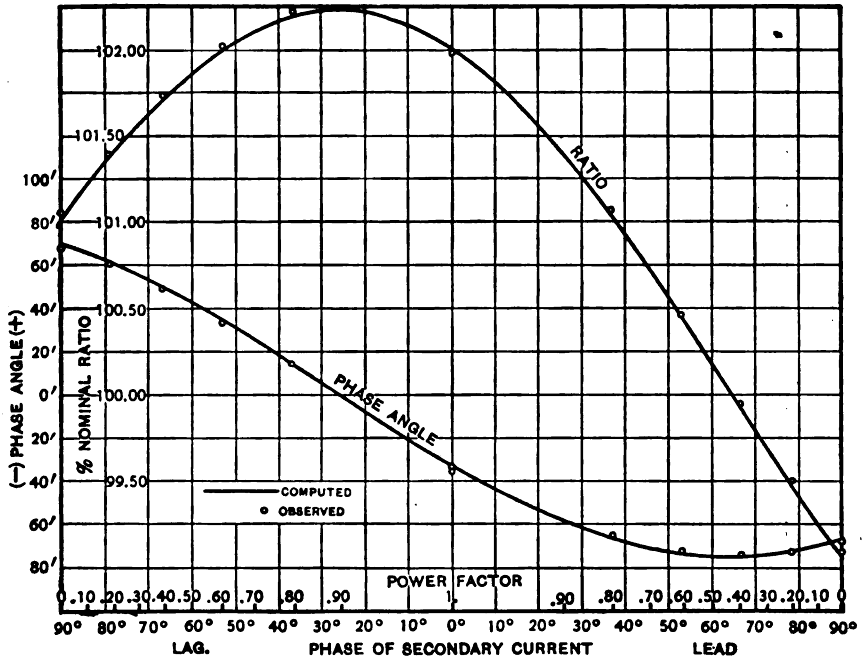

Fig. 5.—*Ratio and phase angle of a 5 kva. 1100/110 volt transformer at normal voltage*

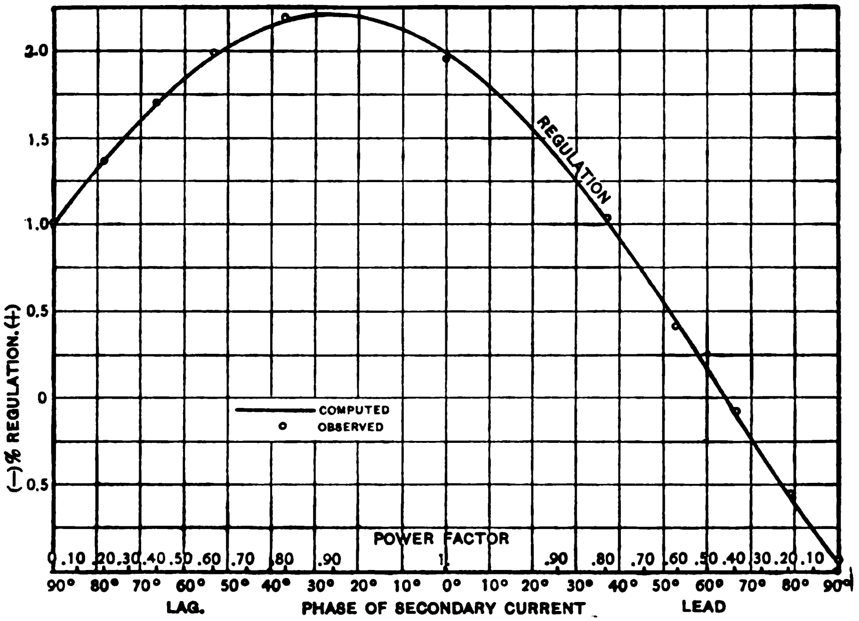

Fig. 6.—*Ratio and phase angle of a 5 kva. 1100/110 volt transformer at excess voltage*

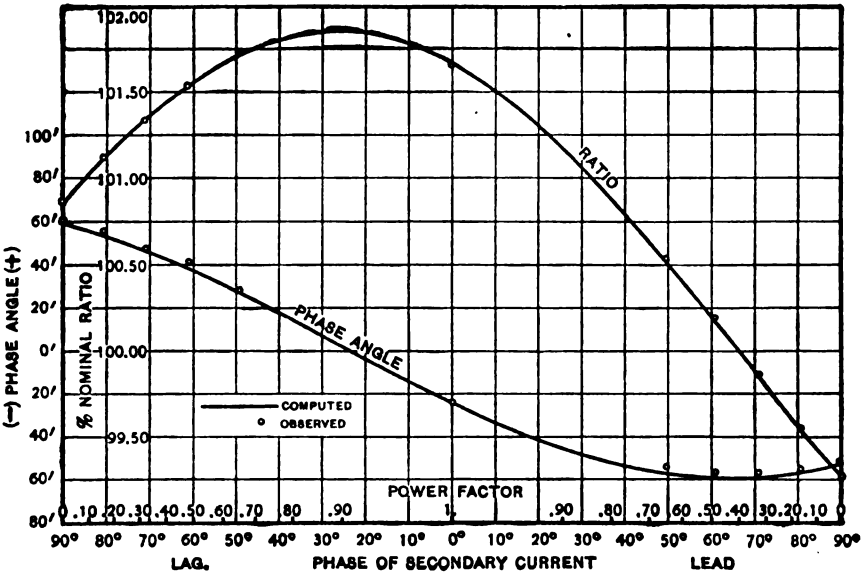

Fig. 7.—*Ratio and phase angle of a 5 kva. 1100/110 volt transformer at excess voltage*

operating characteristics, the accuracy being limited by the errors of measurement and not by theoretical errors.

The applications of these formulas to engineering problems do not come within the scope of this paper.[6]

It is to be hoped that tests along the lines of those here described may be carried out with widely differing types and sizes of transformers by laboratories, such as those of the manufacturing companies, which have the necessary facilities, in order that the adequacy or the limitations of the formulas may be definitely settled.

WASHINGTON, July 11, 1913.

NOTE.—Since the foregoing was written the attention of the standardization committee of the American Institute of Electrical Engineers has been called to the ambiguity in the interpretation of Rules 65, 65a, 67, 68, 69, 70, and 197, and they have officially decided upon the third interpretation given.

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[6] It may be well to mention a point which is sometimes overlooked in paralleling transformers. Two transformers may have the same regulation and the same no-load ratio and still, when connected in parallel, have a very considerable circulating current caused by inequality of phase angle.

MELTING POINTS OF SOME REFRACTORY OXIDES

By C. W. Kanolt

A previous paper[1] dealt with the melting points of commercial refractory materials; the present work is on the melting points of pure oxides. Results obtained with magnesia, lime, alumina, and chromium oxide are given. Although numerous oxides are used as refractory materials, as furnace linings, in the Nernst filament, the Welsbach mantle, and the limelight, and in the laboratory, the melting points of but very few have been known within several hundred degrees. Many of the published determinations are quite uncertain. For example, some determinations would indicate that lime and magnesia are more fusible than alumina, which can easily be demonstrated to be untrue, for alumina is readily fused in the oxyhydrogen flame, while pure lime and pure magnesia are infusible in it, at least under ordinary conditions.

The principal difficulties encountered in the accurate determination of the melting points are the production of very high temperatures uniform over a sufficient space and controllable; the supporting of the oxide in the furnace without its contamination by the material used as a support; the avoidance of smoke, which would interfere with the measurement of temperature by an optical pyrometer; and finally, the accurate measurement of the temperature.

The furnace used was an Arsem graphite resistance furnace,[2] with some minor modifications. This furnace was designed to be used with a vacuum, which prevents the oxidation of the graphite and diminishes the heat losses. The vacuum has also a great advantage in the measurement of high temperatures, as it prevents the formation of smoke. With the use of the vacuum, the furnace is capable of giving temperatures over 3000° C., but when an attempt was made to melt oxides in a vacuum in this furnace it was found that when the temperature reached about 2200° there was an electric discharge from the ends of the heater to the graphite shield, which soon amounted to a short circuit. This is probably a phenomenon of the same sort as the Edison effect. It has been shown by Pring and Parker[8] that the electric discharge from heated carbon is very much less if the carbon is pure than if it contains a small amount of impurity. From this it appears that impurity in the graphite was probably responsible for the discharge in the Arsem furnace. Perhaps the discharge could have been prevented by purifying the graphite of the heater, but as the vaporization of the oxides heated would soon contaminate it again, the procedure would probably be of little use. The discharge can be avoided by using heaters of very low resistance, making it possible to introduce the requisite power at a very low voltage, but this has other disadvantages. The discharge can also be avoided by working at atmospheric pressure, with the concomitant difficulty of the presence of smoke. This procedure was found to be necessary in many cases, for when lime and magnesia are heated in a vacuum they vaporize completely before the melting point is reached.

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[1] B. S. Tech. Papers, No. 10, 1912.

[2] Arsem: J. Am. Chem. Soc., 28, p. 921, 1906; Trans. Am. Electroch. Soc., 9, p. 153, 1906.

With the use of atmospheric pressure considerably more power is required to reach the same temperature, and as the supply of power available was limited it was necessary to change the construction of the furnace somewhat before the higher melting points could be reached. The heater was made of somewhat smaller diameter, as shown at E, Fig. 1, and a second shield for heat insulation, F, was placed within the shield G, supplied with the furnace. The inner shield was filled with powdered graphite, while the outer shield, which of course does not reach so high a temperature, was filled with powdered shrunk magnesia. After this arrangement had been used for some time it was found that the outer shield was badly cracked, apparently as the result of the expansion of the magnesia.

A glass window, H, was substituted for the mica window supplied with the furnace. The glass was attached by a mixture of

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[8] Pring and Parker: Phil. Mag., 23, p. 192, 1912.

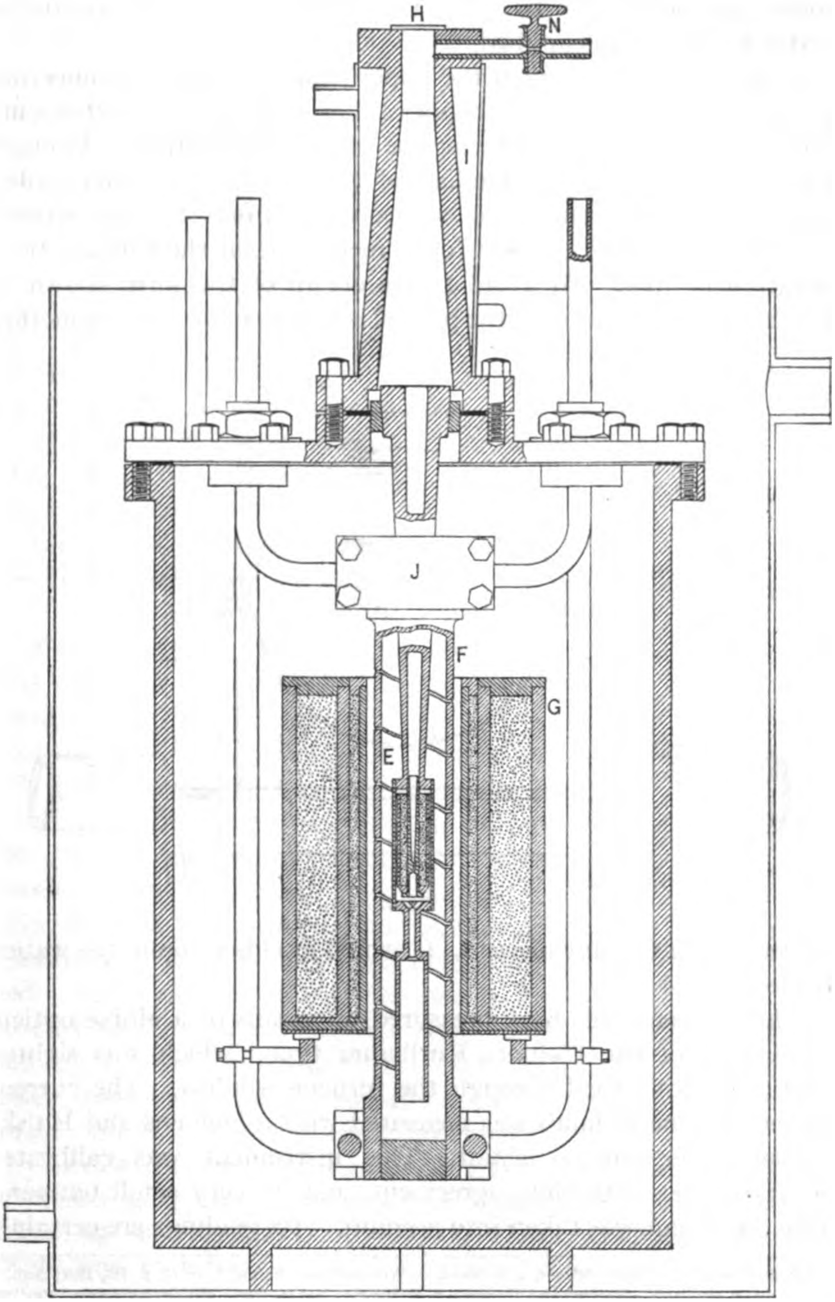

Fig. 1

rosin and beeswax. To keep this material cool an additional water jacket, I, was applied.

A small improvement in the upper copper clamp, J, connecting the heater with one of the copper tubes carrying the electric current and the cooling water, may be worthy of mention. As originally constructed, only one-half of this clamp was water-cooled directly, the other half being connected to it only by steel screws. This uncooled half is likely to be melted when the furnace temperature is high. To avoid this a clamp of the form shown in Fig. 2 was used. In this, the part K is kept cool by the conduction of heat along the side pieces L, L, which fit closely upon the water-cooled half M.

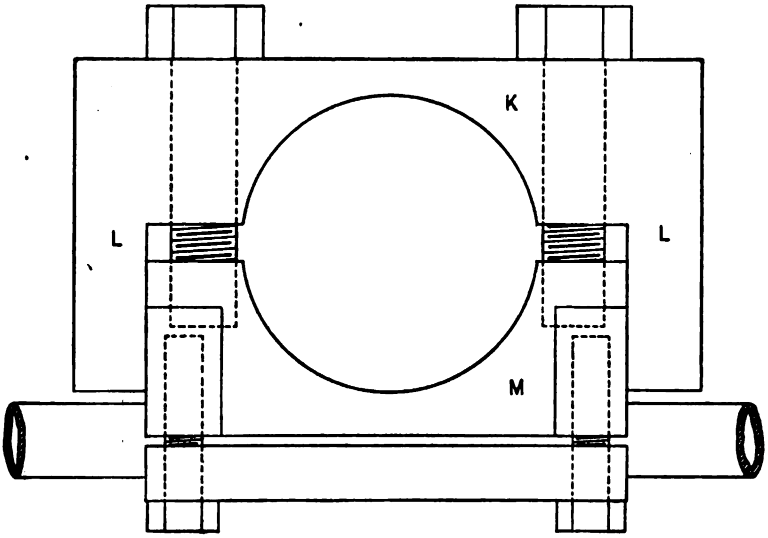

Fig. 2

The temperatures were measured by means of a Morse optical pyrometer of the Holborn-Kurlbaum type,[4] which was sighted vertically downward through the furnace window. The current in the pyrometer lamp was measured with a Siemens and Halske milliammeter with a shunt. This instrument was calibrated several times, with close agreement, and its very small temperature coefficient was taken into account. Its readings are certainly reliable to 0.001 ampere and probably to 0.0005 ampere. The pyrometer lamps had been thoroughly aged and were calibrated against the following melting points:

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[4] Holborn and Kurlbaum: Sitzber. d. k. Akad. d. Wissensch. zu Berlin, June 13, p. 712, 1901; Ann. d. Phys., **10**, p. 225, 1902. Waidner and Burgess: B. S. Reprint No. 11, 1904. Mendenhall: Phys. Rev., **33**, p. 74; 1911. Henning: Zs. f. Instrumentenkunde, **30**, p. 61, 1910.

Material	Melting point
	°C.
Antimony	630
Copper-silver eutectic	779
Silver	960.5
Copper	1083
Diopside	1391

These materials were melted in the Arsem furnace in graphite crucibles, similar to that shown in Fig. 3, but entirely closed at the top to prevent contamination. Heating or cooling curves were plotted. This method has already been described.[5]

In the present work some crucibles were used in which the inner tube was enlarged at the bottom in order to form a better black body, but no difference could be detected between the results obtained with this form and with a cylindrical tube.

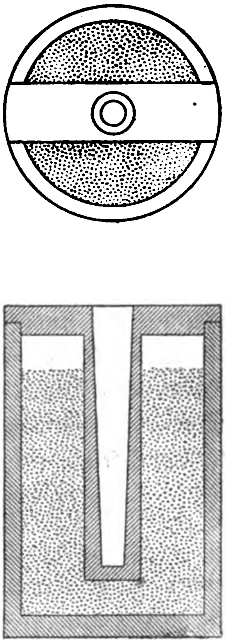

Fig. 3

Diopside has been added to the list of materials previously used in order to make the calibration at the highest temperatures more reliable. There are very few materials melting between the melting point of copper and the working limit of the pyrometer lamps, the melting points of which have been accurately determined. The melting point of diopside is very near this working limit. It has been determined by Day and Sosman.[6] The sample of diopside used was kindly furnished by Dr. Sosman. Since it is not desirable to use platinum crucibles in the Arsem furnace, the diopside was melted in Acheson graphite. This has no observable action upon diopside at its melting point. As a check upon this some diopside was maintained near its melting point in a graphite crucible for about four hours, while a series of determinations of the melting point was made. No change in the melting point could be detected. A change of 1° would probably have been observable. After the pyrometer lamps, which had previously been calibrated at the lower temperatures, had been calibrated at the diopside point, recalibration at lower temperatures lead to the suspicion that they had been changed by the high temperature, although the change was small. To avoid uncertainty from this cause the lamps were completely recalibrated at the four lower points after calibration at the diopside point. Thereafter they were never heated above 1300°.

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[5] Kanolt: B. S. Tech. Papers No. 10.

[6] Day and Sosman: Am. J. Sci., **29**, p. 93, 1910.

The relation between pyrometer lamp current and temperature was expressed by an equation of the form, $C = a + bt + ct^2$, which could be made to coincide closely with all five points of calibration.

As the temperatures to be measured were far above the working limit of the pyrometer lamps, it was necessary to interpose absorption glasses between the pyrometer and the furnace. In order to calibrate these glasses a graphite crucible was placed in the Arsem furnace, the interior of the crucible forming a field of very uniform brightness. A steady current was passed through the furnace and the temperature allowed to become stationary. Measurements of the apparent temperature were then made alternately with and without the interposition of the absorption glass or combination of glasses to be calibrated. If T_1 is the absolute temperature as observed without the glass, and T_2 is the apparent absolute temperature observed with the glass, the following relation is easily deduced from the Wien radiation law:

$$\frac{1}{T_2} - \frac{1}{T_1} = A$$

where A is a constant for monochromatic light. The values of the constants of Wien's law do not enter into the work. The difference between the Wien radiation law and the Planck law in the visible spectrum is entirely insignificant.

In some cases a single absorption glass was used; at the highest temperatures it was necessary to use two. The values of A for two or more glasses in series should be equal to the sum of the values for the individual glasses. Theoretically, the double reflections between the surfaces of the different absorption glasses, and also between the absorption glasses and the furnace window, should cause a variation from this relation, but it was found by calculation that for the particular combinations used the net result of these small effects was quite negligible. However, the first calibrations of two glasses in series gave values of *A* somewhat less than the sum of the values for the individual glasses. Similar discrepancies were obtained by Waidner and Burgess [7] in their work on the temperature of the arc. Such results may be caused by the use of light which is not monochromatic. In the present work the newer kind of Jena red glass, No. 4512, was used, and this has so narrow a transmission band that the error from this source can not be large. Calibrations made with Jena red glass No. 2945, which is less nearly monochromatic, gave greater discrepancies. The cause of the discrepancies remaining when the better red glass was used was found in the lag of the pyrometer lamps. These lamps, which were furnished by the makers of the pyrometer, have filaments about 0.17 mm. in diameter and measuring 5 mm. in length of loop, or 10 mm. in total length. With such short filaments several minutes are required for the lamp to approach sufficiently near to temperature equilibrium for the most accurate work. This is because with short filaments a considerable proportion of the heat is lost by conduction along the leads, and the temperature of the lamp does not become stationary until temperature equilibrium has been reached in the leads. With lamps having longer filaments a greater proportion of the heat is lost by radiation and the lag is much less. The lag made no considerable difference in the calibration of the lamps, for in this case the lamps were maintained at or near the temperature of the fixed point long enough for equilibrium to be reached. But in the calibration of the absorption glasses by the method first used, it was necessary to change the lamp temperature at frequent intervals, the amount of the change being greatest with dense absorption glasses. To avoid this difficulty two pyrometer lamps were used, each having its own regulating resistance, but so arranged that they could be quickly interchanged in the pyrometer, and could be alternately put in series with the same ammeter. Each lamp was maintained at approximately constant temperature, one being used to measure the temperature of the furnace, the other to measure the apparent temperature observed through the absorption glasses. With the use of this apparatus good agreement was obtained between the observed values of A for two absorption glasses in series, and the values calculated from the values for the individual glasses, the remaining discrepancy being such as could be produced by errors of less than 1° in temperature measurement.

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[7] B. S. Reprint No. 8, p. 116; 1904.

The glass furnace window absorbed and reflected a small amount of light, and it was necessary to apply a correction for this. To determine the value of A for the window, a second glass was cut from the same piece, and determinations of the apparent furnace temperature were made alternately with and without the interposition of this second piece. A very small correction was applied for the double reflection between the two pieces.

As a check upon the whole pyrometric apparatus a series of determinations of the melting point of platinum was made. The platinum was melted in tubes made of a mixture of magnesia and alumina,[8] obtained from the Königliche Porzellan-Manufactur, Berlin. These tubes were inserted in a vertical iridium furnace. Both heating and cooling curves were obtained. The black-body conditions were very good, the platinum being entirely invisible. Usually 3 to 4 grams of platinum were used. The platinum was the purest obtainable from Heraeus, and of the same kind as that used by several investigators in the determination of the melting point of platinum.[9]

The results are included in Table 1. The weighted mean, 1755°, is identical with the value accepted as the melting point by the Bureau of Standards.

TABLE 1

Melting Point of Platinum

Pyrometer lamp	Absorption glasses	Melting point	Weight
		°C	
171	4248A1	1745	1
171	4248A1	1751	3
171	4248A1	1753	3
171	4248A1+4247B	1761	3
171	4248A1+4247B	1759	3
Weighted mean		1755	
Average deviation		5	

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[8] Heinecke: Zs. angew. Ch., **21**, p. 687; 1908.

[9] Cf. Waidner and Burgess, B. S. Reprint No. 55, p. 183; 1907.

The problem of avoiding smoke when the oxides are not heated in a vacuum has received very little attention in previous work, and is probably responsible for several low results. It was found that errors from the presence of smoke could be avoided by introducing into the oxide to be melted a tube of suitable material into which the pyrometer was sighted, and driving from this tube any smoke that might enter through pores or joints by a gentle current of gas. Very good black-body conditions were obtained within such tubes. With this apparatus it was impossible to see the oxide while it was in the furnace, but as all melting points were determined by heating curves this was not necessary, and the determinations could be checked by the examination of samples that had been heated to temperatures slightly below that obtained for the melting point, and also of samples heated slightly above this temperature. A somewhat different method has also been used in determining the melting point of lime. The lime itself was made into a tube, the upper end, by which it was supported, being at a low temperature, while the lower end extended into the hot part of the furnace. The tube was kept free from smoke by a gentle current of hydrogen, which passed out through an oblique opening at the bottom. The pyrometer was sighted into the tube, and a heating curve was plotted. This method has the advantage of avoiding all contact of foreign substances with the material being melted. It is believed that it will prove of value in work upon other substances.

The magnesia used was obtained from the J. T. Baker Chemical Co. The maker's analysis is as follows:

	Per cent.
CaO	None.
Al_2O_3	0.0002
Fe	0.0005
CO_2	0.130
Cl	0.275
HNO_3	None.
SO_3	—0.001

As it is difficult to completely free magnesia from lime, and as it was found that magnesia sold as free from lime may contain considerable quantities of it, a spectroscopic test for lime was made on this sample, but none was found. It was found by experiment that the test was sensitive at least to 0.01 per cent of lime. The carbon dioxide, chlorine, and sulphur trioxide indicated in the maker's analysis would of course be vaporized before the magnesia reached its melting point.

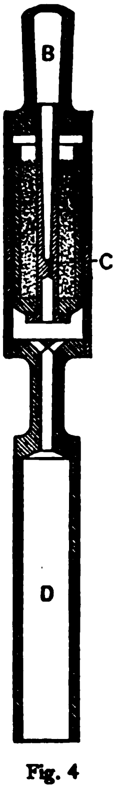

Fig. 4

The magnesia was melted in graphite crucibles, for it forms no carbide at high temperature.[10] It is probably the only refractory oxide having this property. It does react with carbon with the formation of carbon monoxide and magnesium vapor,[11] but this introduces no contamination into the magnesia. It causes a rapid loss of magnesia, especially after fusion, but it was found possible to heat the furnace rapidly enough to determine the melting point before the magnesia had all gone, although it was not practicable to obtain cooling curves, and there was often no magnesia left when the furnace had cooled. All experiments were made at atmospheric pressure in a mixture of carbon monoxide and nitrogen obtained by drawing air through a bed of hot charcoal. When a vacuum was tried the magnesia vaporized before the melting point was reached, even when the magnesia was not heated in contact with carbon, but was in the form of a rod supported by one end which was at a low temperature.

The apparatus used for magnesia is shown in detail in Fig. 4, and is shown in position in the furnace in Fig. 1. It was made entirely of graphite. The magnesia is shown at A. The pyrometer was sighted down the tube B. A mixture of carbon monoxide and nitrogen was introduced into this tube through the stopcock N (Fig. 1), and passed down through a very small hole C, which was drilled obliquely to avoid its appearing as a dark spot in the field of the pyrometer. The gas, together with the smoke from the magnesia, then passed down through the tube D. The object of this tube was to prevent the gases from coming directly in contact with the hot part of the heater, as this would burn a thin place in the heater. With the use of this apparatus one heater would last for about four experiments, barring accidents. The upper part of the tube D was made small to diminish heat conduction; the lower part was made larger to avoid clogging with magnesia. Gas was driven through the apparatus at the rate of about 5 cc per second, measured cold, or about 50 cc per second at the temperature of the apparatus. In order to determine whether this produced an appreciable cooling effect, the empty apparatus was heated to about 2500° and the temperature allowed to become constant. As there was no magnesia in the furnace there was no perceptible smoke. A number of temperature measurements were then made without a gas current, then with the gas turned on, and again with the gas turned off. The measurements were in close agreement and indicated that the cooling produced was not more than 5°. A confirmation of this was obtained in another way in the work on alumina.

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[10] Cf. Moissan: Comptes rendus, **126**, p. 302; 1898.

[11] Watts: Trans. Am. Electroch. Soc., **11**, p. 279; 1907.

The magnesia that had been fused was colorless, fairly transparent, and of a compact crystalline structure.

The results obtained with magnesia are given in Table 2.

TABLE 2

Melting point of magnesia, obtained with apparatus shown in Fig. 4

Pyrometer lamp	Absorption glasses	Melting point	Weight
		°C	
171	4248A1+4247B	2808	3
171	4248A1+4247B	2780	2
171	4248A1+4247B	2818	3
147	4248A2+4247A	2771	1
147	4248A2+4247A	2799	2
147	4248A2+4247A	2799	3
Weighted mean		2800	
Average deviation		13	

The lime used was obtained by the ignition of some calcium carbonate, obtained from the Baker & Adamson Chemical Co. The maker's analysis is as follows:

Solution in HCl	Clear
H_2S metals	Nil
Cl	0.0004%
Nitrate	Nil
Na and K	Nil
Sulphate	Nil
Mg	Trace

Since lime readily forms carbide when heated to high temperatures in contact with graphite, the use of graphite crucibles, as with magnesia, was out of the question. In place of graphite tungsten was tried. Tungsten is readily obtainable in the form of a fine powder. It is possible to make rods or thick-walled crucibles of this by moistening it with water, compressing it in a mold, and then removing it from the mold and heating it to about 1800° C or higher without contact with air. At this temperature the tungsten powder sinters to a porous mass, the hardness of which depends upon the temperature to which it has been heated. But if thin-walled or comparatively frail forms are molded, it is practically impossible to remove them from the mold before heating without breaking or distorting them. This difficulty may be overcome by using a mold the outer parts of which are made of graphite, while the inner parts, by which the inner surfaces of tubes or crucibles are formed, are made of metal. These inner parts are readily removed from the tungsten. The graphite part of the mold and the tungsten in it are then heated together to 1800° to 2000°, after which the tungsten can be removed from the mold. Tungsten readily combines with carbon at these temperatures, and if the heating is continued for any length of time the tungsten adheres to the mold and may become badly contaminated. However, if the tungsten is heated very rapidly to the sintering temperature and then immediately cooled, as can readily be done in the Arsem furnace, it takes up but little carbon and does not adhere to the mold. Tungsten can be molded into almost any shape in this way. The product is very porous and readily absorbs thin liquids, which would be a disadvantage for many purposes; but it does little harm in the determination of melting points, for after a material has been melted and its melting point determined, it usually matters but little what happens to the melted material. If the tungsten is sintered at a comparatively low temperature it can afterwards be shaped by grinding and to some extent by cutting, although it soon dulls a steel tool.

Three melting-point determinations were made in an apparatus similar to that used for magnesia (Fig. 4), but having the crucible and the inner tube made of tungsten. These results were in excellent agreement. The tungsten parts usually melted as soon as the lime melted. This may have been the result in part of the contamination of the tungsten by carbon or the presence of other impurity, but it was noticed that the melting of the crucible appeared to begin on the inside, indicating that it was the result of the contact of tungsten with fused lime. This suggested that if the lime contaminated the tungsten, the tungsten might also contaminate the lime and change its melting point. In order to check the results so obtained the lime tube method was used. This apparatus is shown in Fig. 5.

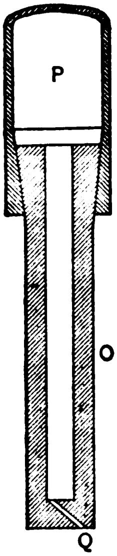

Fig. 5

The lime tube O is connected by a taper joint to the graphite tube P, which is supported from the top of the furnace. The hydrogen driven into the tube to remove smoke passes out through the small oblique opening Q. It is quite likely that the gas current produced some cooling in this case, for lime is a poorer conductor of heat than the graphite or tungsten used in the inner tubes in previous experiments. This cooling could cause no error in this case, as it is produced directly in the material to be melted. A gentle gas current was found to remove smoke quite effectively. The results obtained in this way agreed entirely with those obtained in tungsten crucibles. A test for calcium carbide was applied to lime from the lower end of a lime tube after it had been heated almost to the melting point, but no carbide could be detected. The test was probably sensitive to 0.01 per cent. This lime was perfectly white. The upper parts of the tubes, which did not reach so high temperatures, were always gray after heating and contained small amounts of carbide. It is probable that at the temperature of fusion any carbide that was formed at lower temperatures reacted with the lime forming carbon monoxide and calcium vapor.

The results obtained with lime are given in Table 3.

TABLE 3

Melting Point of Lime

Pyrometer lamp	Absorption glasses	Melting apparatus	Melting point	Weight
			Deg.	
171	4248A1+4247B	Fig. 4 (tungsten)	2565	1
171	4248A1+4247B	do	2575	1
171	4248A1+4247B	do	2575	1
171	4248A1+4247B	Fig. 5	2571	3
171	4248A2+4247A	do	2572	3
171	4248A2+4247A	do	2575	2
Weighted mean.			2572	
Average deviation.			3	

The alumina used was obtained from Eimer & Amend. The maker's analysis is as follows:

	Per cent.
Iron	0.001
Calcium	None.
Silica	—.001
Chloride	.005
Sulphate	—.001

The first determinations of its melting point, made before the tungsten crucibles had been prepared, were made in graphite. Alumina forms a carbide at its melting point, but the reaction is not a rapid one. There appeared to be none formed until after the alumina had melted and had remained for a time in contact with carbon. The alumina rapidly diminished in quantity after melting. How much of this loss was the result of the vaporization of alumina and how much the result of reaction with the graphite with the formation of aluminum vapor was not determined. Alumina that had remained in the melted condition but a short time was white and of a compact crystalline structure. When maintained in a fused condition for some time it became grayish in color. Any changes that may occur after the fusion of the alumina cause, of course, no error in the melting-point determination. After tungsten crucibles had been prepared determinations were made in tungsten with the same results. Alumina can be melted in a vacuum sufficiently good to prevent smoke without vaporizing too rapidly. Experiments were made at a pressure of about 2 mm of mercury and also at atmospheric pressure. In the latter case apparatus of the form used with magnesia (Fig. 4) was used. In working with a vacuum, crucibles of the form shown in Fig. 3 were used. As these crucibles were partly open at the top the melting material could be seen at the same time that the temperature determinations were made with the pyrometer sighted down the inner tube. The close agreement between results obtained in a vacuum and at atmospheric pressure in a current of gas is further evidence that the gas current does not cool the inner tube appreciably.

The results obtained with alumina are given in Table 4.

TABLE 4

Melting Point of Alumina

Pyrometer lamp	Absorption glasses	Melting apparatus	Melting point	Weight
			°C	
171	4248A1+4247B	Fig. 3; graphite; in vacuum	2045	3
171	4248A1+4247B	Do	2053	1
171	4248A1+4247B	Fig. 4; graphite; with gas	2053	2
171	4248A1	Do	2041	2
171	4248A1+4247B	Fig. 3; graphite; in vacuum	2055	3
171	4248A1+4247B	Do	2046	2
171	4248A1	Fig. 3; tungsten; in vacuum	2049	2
171	4248A1	Do	2055	3
Weighted mean.			2050	
Average deviation.			5	

The chromium oxide (Cr_2O_3) used was obtained from Eimer & Amend. The maker's analysis is as follows:

	Per cent.
Iron	0. 01
Chromate	Trace.
Sulphate	0. 005

It was melted in a vacuum in crucibles of the form shown in Fig. 3. When graphite crucibles were used there was little reduction until the oxide began to melt; then there was a vigorous reaction. When tungsten crucibles were used the melted oxide soaked into the porous tungsten to a considerable extent. The results obtained with the two crucible materials were in agreement. They are given in Table 5.

TABLE 5

Melting point of chromium oxide, obtained with crucibles of the form shown in Fig. 3

Pyrometer lamp	Absorption glasses	Crucible material	Melting point	Weight
			°C	
171	4248A1+4247B	Graphite	1990	3
171	4248A1+4247B	Tungsten	1982	1
171	4248A1+4247B	do	1979	2
171	4248A1	Graphite	1991	1
171	4248A2	Tungsten	2000	3
Weighted mean.			1990	
Average deviation.			6	

Some typical heating curves are shown in Fig. 6. There was no appreciable difference in curves obtained with different oxides. Usually there was a small break in the heating curve at a temperature a little below the melting point. It is believed that this small lag in the heating was always present, although it was not always certainly observable. It undoubtedly occurs at the instant that melting begins on the outside of the mass of material. Since the oxides are comparatively poor conductors of heat and since the rate of heating was necessarily rather rapid, the temperature of the inside of the mass where the temperature was measured lagged appreciably behind the temperature of the outside, until the outside began to melt, after which the temperature of the inside rose to the melting temperature already reached on the outside, and a distinct break in the curve corresponding to the true melting point followed. This explanation is supported by observations made when the open crucibles shown in Fig. 3 were used. The beginning of melting on the outside of the mass was sometimes observed at the same time that the small preliminary break in the heating curve occurred.

In Table 6, the results obtained are compared with determinations by previous investigators. It will be noted that the older values for the melting points of magnesia and lime are very much lower than the results of this investigation, although Greenwood [12] records the use of magnesia crucibles as high as 2500°. In the work of Hempel, Goodwin and Mailey, and Lampen there seems

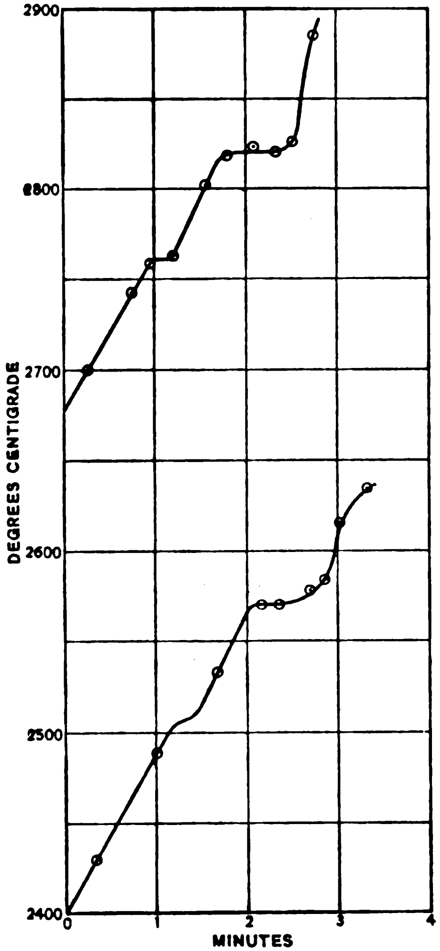

Fig. 6.—*Heating curves obtained with magnesia (upper curve) and lime (lower curve).*

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[12] Proc. Roy. Soc. (A), 82, p. 396; 1909.

to have been little or no precaution taken against the presence of smoke.

TABLE 6

Material	Melting point, Bureau of Standards	Previous determinations
	°C.	
MgO	2800	2250 Hempel [13]
		1910 Goodwin and Malley [14]
		2000 Lampen [15]
		1980–2023 Mendenhall and Ingersoll [16]
		Over 2500 Ruff [17]
CaO	2572	1900 Hempel [13]
		Over 2450 Ruff [17]
Al_2O_3	2050	1800 Hempel [13]
		2050–2100 Saunders [18]
		2010 Ruff [17]
Cr_2O_3	1990	2060–2080 Ruff [17]

[13] Ber. Inter. Kongress Angew. Chem., **1**, p. 715; 1903.

[14] Phys. Rev., **28**, p. 22; 1906.

[15] J. Am. Chem. Soc., **28**, p. 846; 1906.

[16] Phys. Rev., **25**, p. 1; 1907.

[17] Zs. f. anorg. Chem., **82**, p. 373; 1913.

[18] Trans. Am. Electrochem. Soc., **19**, p. 333; 1911.

In the work of Mendenhall and Ingersoll small particles of magnesia were heated upon a Nernst glower. On account of the small amount of material there was probably no considerable amount of smoke, but the magnesia would almost certainly flux with the glower material. None of these investigators have given much attention to the purity of the magnesia, which seems to be more difficult to obtain pure than lime or alumina.

Ruff and his collaborators have published determinations of a large number of melting points. The full results have appeared since this article was written. The value quoted above for chromium oxide (2060 to 2080°) is not presented by Ruff as the true melting point. Lower values were also obtained but were apparently the result of partial reduction.

The writer has obtained preliminary results with other oxides and the work will probably be extended. The method in which the refractory material is made into a tube appears to be the most promising.

Mr. S. E. Moore has rendered valuable assistance in this work.

SUMMARY

The melting points of some refractory oxides have been determined in a graphite resistance vacuum furnace. The temperatures were measured by an optical pyrometer and heating curves were plotted. The production of smoke when some of the oxides were heated was found to be an important source of error, as the smoke interferes with the use of the pyrometer. Means by which this difficulty was overcome are described. The following melting points were obtained, the melting point of platinum being determined merely as a check.

Material	Melting point
	°C.
MgO	2800
CaO	2572
Al_2O_3	2050
Cr_2O_3	1990
Pt	1775

WASHINGTON, June 1, 1913.

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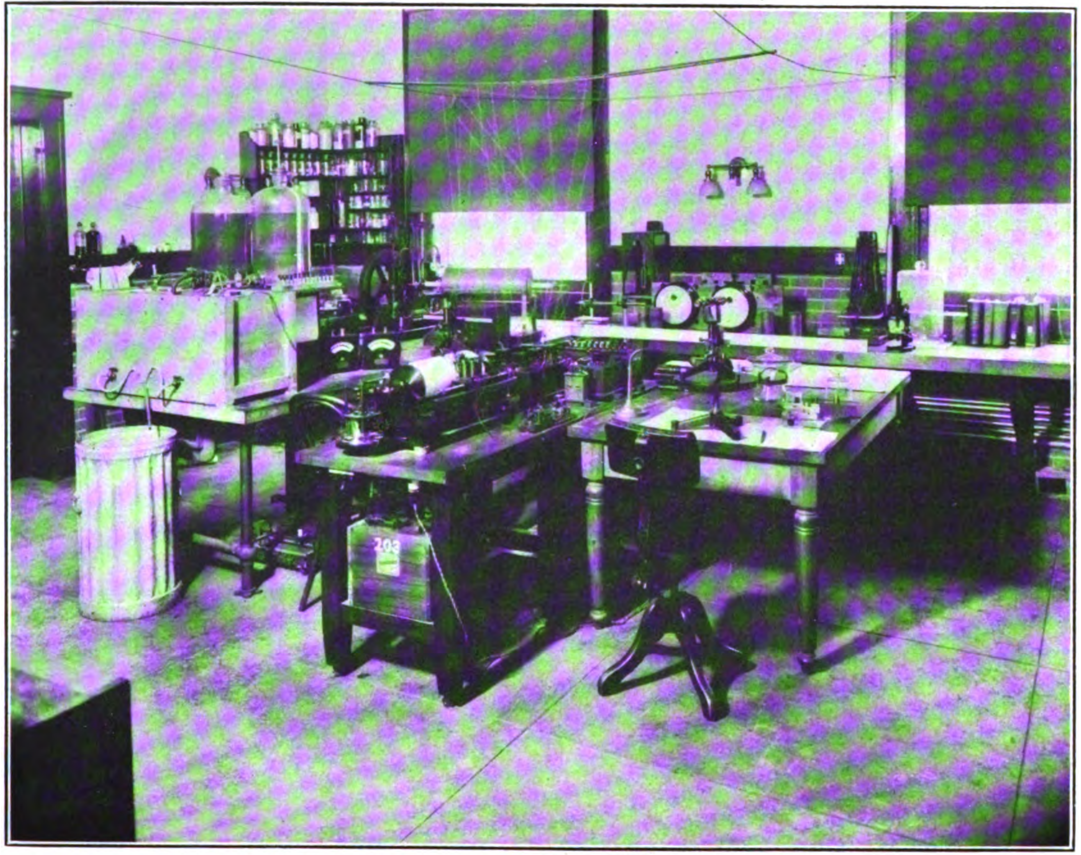

Plate I.—*Photograph of apparatus*

CRITICAL RANGES A2 AND A3 OF PURE IRON

By G. K. Burgess and J. J. Crowe

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INTRODUCTION

The question of the allotropy of iron, in spite of a vast amount of experimental work and perhaps an even greater amount of theorizing, is not yet settled. That there is a definite transformation in iron near 900°, the A3 point, is generally recognized, as well as the fact that the temperature of this transformation is lowered by the addition of carbon and metallic elements. On heating the transformation Ac3 is always found at a higher temperature than the transformation Ar3 on cooling. Whether the A3 transformation is sharp, like the melting point of a pure substance, or extends over a considerable range of temperatures, embracing perhaps as a lower limit the A2 change, appears to be still an open question for pure iron. The nature and identity of the A2 transformation, it would appear from recent publications, has not yet been satisfactorily settled.

In the present paper there is given a critical, historical summary of the experimental investigations of the location of A2 and of A3 in pure iron, together with brief mention of some of the theoretical aspects of the subject, and an account of a series of experiments carried out with several samples of very pure iron which were studied by two methods of thermal analysis in the range 500°C to 1000°C, and which it is believed furnish a contribution of considerable interest as to the location and nature of the A3 and A2 transformations.

Great attention has been given to the details of experimental manipulation and to the preparation of the samples, as it was soon found that some of the discrepancies noted in the work of many experimenters may be traced largely to lack of precautions which we have found essential.

For example, to anticipate somewhat, it is necessary to provide a suitable, practically gas-free furnace, the heating and cooling of which may be regulated to a nicety; to reduce to a minimum the deforming effects on the cooling and heating curves due to the poor conduction of the sample, it must be of a form and mass to pass on its heat rapidly and completely to the thermocouple; and finally, the sample itself should be free from gases, which, if present, further mask the definiteness of the heating and cooling curves. We have also varied within wide limits the several factors which may influence the determination of the exact location and shape of the transformation ranges, especially the mass and preparation of sample, rate of heating and cooling, design of furnace, and finally, as nearly as it is experimentally possible, we have worked with a substance approaching pure iron, free from occluded gases and other impurities and contained within a vacuum.

A preliminary notice of some of the experiments carried out in 1911 and 1912 has already been published,[1] but since this work the experimental method has been greatly improved and several newly prepared samples investigated.

The methods of this investigation are described in considerable detail, as they are the same now being used in a new study of the iron-carbon system and because they are believed to be of some interest in themselves.

THEORIES OF THE ALLOTROPY OF IRON

Several explanations have been offered for the existence and nature of the transformations in iron, and the discussion of this subject has usually been linked with the transformations occuring in the iron-carbon system. For the consideration of *pure* iron, however, it seems simpler and sufficient to forget for the moment the iron-carbon system which has no more relation to pure iron than, say, the iron-manganese or iron-sulphur series of alloys. Furthermore, if there were agreement as to the facts concerning these transformations, the establishment of a satisfactory explanation in terms of well-known physicochemical principles should not be difficult. But we are in the presence of a double uncertainty, both as to facts and as to theory. Until the facts are well established and recognized any theory can be at best only a working hypothesis.

Briefly stated, the current hypotheses regarding the A3 and A2 transformations in iron are:

1. The critical points A3 and A2 divide iron sharply into three allotropic forms, γ-iron above A3, β-iron between A3 and A2, and α-iron below A2.

2. The critical point A3 is the seat of an allotropic change, but the A2 point is not, the transformation at A2 being associated

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[1] J. Iron and Steel Institute, 87, p. 335, 1913; J. Washington Academy, 3, p. 329, 1913.

mainly with the loss of magnetism which is accompanied by a small thermal change. Hence, there is no β-iron according to this theory, and the A2 transformation may be abrupt or spread over a considerable temperature interval as experiment may require

3. The critical range A2 is not independent of A3 but forms a part of the A3 transformation. Here, again, we have no β-iron, but to account for an evolution of heat on cooling at A2 requires assumptions regarding the mutual solubility of γ-iron in α-iron, and even the simultaneous existence in meta-stable equilibrium of two kinds of molecules of the same substance.

This last type of physicochemical equilibrium has been studied both theoretically and experimentally by Smits for several chemical systems, and for any particular case may be verified by noting the change in location of the transformation temperatures with rate of cooling.

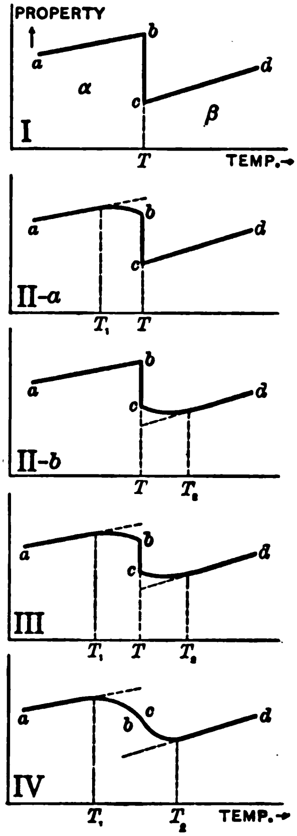

Fig. 1.—*Types of allotropy (Benedicks, Smits)*

Benedicks has put forth a theory of allotropy in which the allotropic change may be of several types,[2] as illustrated in Fig 1. Applied to iron, he would assign Type II*a*, which relegates A2 to the end point of A3 or the temperature at which γ and α irons cease to interact. If A2 can be shown to be constant in position independently of rate of cooling, then Smits' analysis will not apply, and if A2 persists in magnitude and location for heating and cooling through the A2 range and holding the sample a long time below A3 but above A2, Benedicks's hypothesis becomes of little meaning.

There are various other minor modifications of the above three hypotheses, all of which have been useful and perhaps none of which is without value in furnishing some part of a satisfactory explanation of the transformations in iron.

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[2] These types may also be deduced from the theory of Smits.

PREVIOUS DETERMINATIONS OF A2 AND A3 IN IRON

We shall pass in review briefly the experimental evidence as to the existence and nature of transformations in iron at A2 and A3, as shown from observations on the physical properties of iron, including dilatation, electrical and magnetic changes, specific heat, heat evolution and absorption, crystalline structure, and deformation under stress. As we are dealing with a single element, purely chemical changes would not be expected to shed any light on the question of such transformations, and there appear to be no strictly chemical data bearing on the subject, except some inconclusive work on the dissolving power for carbon.

In quoting the numerical values of the temperatures assigned to transformations as noted by the several observers (see Tables 1 and 2), it should be borne in mind that there are considerable discrepancies in the temperature scales used, and sometimes the method of experimental operation leads to incorrect temperatures of the phenomena measured. No general attempt is made here to correct the temperatures as given by the several observers, as for the most part such correction would be extremely uncertain. This uncertainty is further enhanced in some cases by the impurity of the samples of iron operated upon.

In this historical summary we are more concerned with the qualitative aspect of the transformations—their very existence, in fact—than their exact location, which latter we believe is most exactly defined by our own experiments.

Critical Ranges as Determined by Expansion.—Both from the work of Charpy and Grenet and of Broniewski, observations on the expansion of iron give no indications of the existence of A2. The former places the contraction observed as lying in the interval 860° to 890° for iron, with 0.03 carbon, while the latter finds it above 950° for electrolytic iron.

The disagreement is here great enough to again raise the question, as was done by Le Chatelier in 1899, of the rate and other conditions of heating, and also whether the sensibility of the methods used was great enough to detect A2. Even its nonexistence, in so far as expansion is concerned, would prove only that iron immediately above and below A2 has the same coefficient of expansion, or simply that the A2 transformation is unaccompanied by appreciable change in volume—a not unreasonable possibility. The more recent experiments of Rosenhain and Humfrey would appear to indicate a slight volume change accompanying A2.

Critical Ranges by Thermoelectric Observations.—This method of operation is open to the serious objection, for the exact location and description of critical ranges, that the iron which forms one element of a thermocouple must be partly in a hot region and partly in a cold. The reactions due to whatever transformations take place will be progressive along the iron and thereby may mask any transformation on heating, for example, after the one taking place at the lowest temperature.

Using a Fe-Cu thermocouple, Broniewski finds for electrolytic iron a hazily defined point of inflexion at 730° and another at 950° on heating (or at 850° for 0.07 per cent carbon), but with a Fe-Pt couple he is able to detect only the point at 1020° which Müller claims is due to hydrogen. Both Harrison and Belloc fail to get any thermoelectric discontinuity with Fe against either Cu (Harrison) or Pt (Belloc) but appear to find a maximum for the curve of thermoelectric power at about 800°.

Thus, the thermoelectric data on the critical ranges of iron appear to be meager and of little value, and the thermoelectric method can not register transformations sharply except with an indefinitely short furnace, or one having no appreciable length between the inside and outside temperatures along the iron sample.

Critical Ranges in Terms of Crystalline Structure.—There appears to be practical unanimity of opinion concerning the evidence offered by the various investigations (Osmond and with Cartaud, Carpenter and Stead, Rosenhain and Humfrey, and others) concerning the existence of changes of crystalline structure, namely, that the A2 region is not accompanied by any appreciable crystalline change while the A3 transformation in pure iron is so accompanied. All these experiments appear to show there is no crystallographic difference between β and α iron, although there does not appear as yet to be perfect accord as to the nature of the crystalline change taking place at A3.

Critical Ranges as Detected by Mechanical Methods.—The study of the mechanical properties of metals at high temperatures offers very great experimental difficulties, and as far as approximately pure iron is concerned the only experiments which shed any light on the detection of A2 and A3 by mechanical means are those of Rosenhain and Humfrey, who have carried out two series of measurements on tensile strengths, the first of a more qualitative nature in which an iron 99.76 pure, containing 0.03 carbon, was used, and the second, much more elaborate, with iron containing 0.1 per cent carbon. Both series show a distinct discontinuity for the A2 range and for the A3 range. (See Fig. 2.)

Critical Ranges as Given by Electrical Resistance.—The electrical resistance of approximately pure iron at high temperatures has been studied among others by Le Chatelier, Hopkinson, Morris, Boudouard, Harrison, A. R. Meyer, and Broniewski.

The observations show, when plotted as resistance (or ratio of resistance hot to resistance cold, R_t/R_{20}) against temperature, a continuous curve which begins to inflect at temperatures ranging from 700° (A. R. Meyer) to 800° or higher (Le Chatelier, Hopkinson). At about 900° to 950° the curve becomes nearly horizontal, as found by all observers, and according to Broniewski has another inflection at 1020°. This observer, however, took observations with the iron in an atmosphere of hydrogen, but Müller has shown that with electrolytic iron a critical point is obtained thermally in this region only until the hydrogen is removed by successive heatings.

The observations of Meyer appear to have been taken with considerable care on very pure samples of iron, and when plotted as dR/dt against t give a cusp at 700° and are strikingly similar to the magnetic susceptibility curves obtained by Curie and others, as shown in Fig. 2. The observations of Morris, who used iron 99.92 pure, give a sharp maximum for dR/dt at 765°, and Somerville gets one at 750° with an undefined "iron," while Boudouard finds two breaks in the $R:t$ curve, one at 775°, the other at 885°.

As in the case of nickel with a transition point in the region about 370°, the electrical resistance curve appears to anticipate, as it were, the A2 transformation for iron, which as

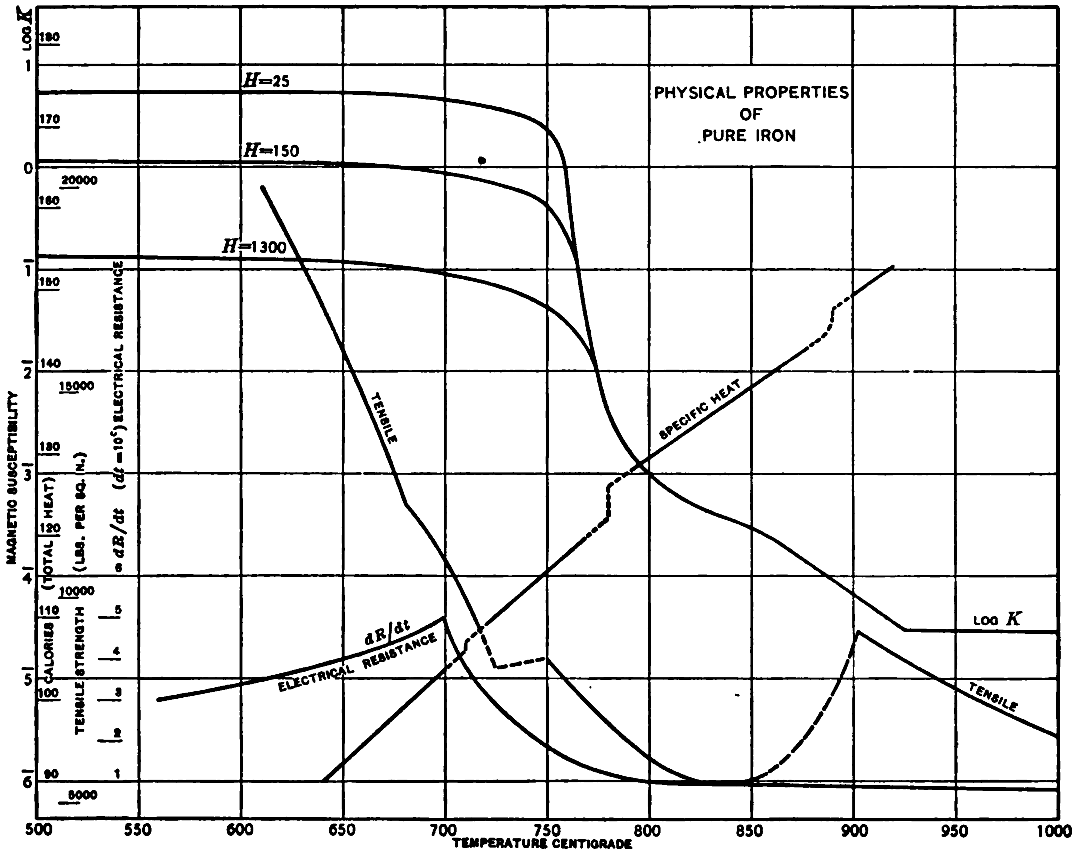

Fig. 2.—*Physical properties of pure iron*

measured by this phenomenon may be considered as starting some 60° or 70° below the maximum; or, in Benedick's nomenclature, is a transformation of Type II*a*. The observations of Broniewski also show a second inflection (for A3?) at about 950°, although, if present, this inflection should have been detected by Morris, Meyer, and others.

Critical Ranges as Determined Magnetically.—Hopkinson, using a wrought iron containing 0.01 per cent carbon and 0.362 per cent of other impurities, mostly slag, finds a cusp in the permeability curve at 775°, the permeability for a magnetizing force of 0.3 falling from 11 000 at 775° to 1 at 785°. With a mild steel containing 0.126 per cent carbon and 0.244 Mn, the peak is at 730° for the same small magnetizing force.

The exhaustive experiments of P. Curie show that the intensity of magnetization (I) is markedly dependent upon the value of the magnetizing force (H) for iron containing only 0.04 per cent carbon, and decreases (for all values of H) at first gradually with rise in temperature and above 700° with increasing rapidity, reaching almost to zero at 750°, where there is an abrupt turn in the I:T curve. Above 750° the I:T curve possesses no considerable variations until 1280° C. The magnetic susceptibility $k = I/H$ (plotted as log k:T in Fig. 2) decreases with great abruptness at about 750°, although the decrease in k begins gradually from below 625° (high values of H decreasing k at lower temperatures than low values of H). There is a further abrupt drop in k, beginning at about 860°, terminating sharply at 920°. Terry, and very recently Honda, find that ferromagnetism disappears on heating and reappears on cooling at 785°. At the laboratories of Schneider & Co. the loss and gain of magnetism are found to be associated with A2 at about 770°.

The magnetic behavior of iron in the region about 750° appears in all respects similar to the behavior of other ferromagnetic substances, such as nickel, cobalt, and magnetite, in the region of their single magnetic transformation points, which for these substances, it is of importance to note, are also transformation regions as measured by other physical properties, such as electrical resistance, thermoelectricity, and thermal or calorimetric effects.

This last is well shown by the experiments of Weiss and his associates, who are able to compute from purely magnetic data obtained at higher temperatures the transformation points by means of the equation k $(T-\theta)=\text{const.}$, and compare them with the values obtained calorimetrically. In this way Weiss and Beck find:

Transformation points $=\theta-273$	Calculated magnetically	Observed calorimetrically
Iron	753°	758°
Nickel	376	376
Magnetite	588	580

Later magnetic observations by Weiss and Foëx, who used less than 0.5 g, place the Curie point, θ, (=A2) at 774° for electrolytic iron, divide the β region into two parts, β_1 and β_2, and locate the transition from β_2 to γ iron with great sharpness at 920°.

Magnetically speaking, therefore, it appears reasonable to claim that the critical range A2 for iron is strictly similar to the transformation taking place generally in ferromagnetic substances as they pass over into the feebly magnetic state. In addition, the iron undergoes a further distinct magnetic modification accompanying the A3 transformation.

Critical Ranges as Determined Calorimetrically.—There have been several determinations of the specific heat of iron at high temperatures but for most of them in the range 700° to 950° the observations are not closely enough spaced to locate the critical ranges with definiteness.

Weiss and Beck were able to identify the Curie point computed from magnetic data with an abrupt change in the specific heat of iron at about 755° to 760° (or A2) but did not go high enough in temperatures to reach A3.

Meuthen, using the vacuum furnace and calorimeter of Oberhoffer, has been able to locate both A2 and A3 with considerable exactness for iron containing 0.06 per cent carbon, in terms of the specific heat. (See Fig. 2.) He places A2 at 770° to 790° and A3 at 880° to 900°. Also A2 remains constant in temperature to the point O in Fig. 3.

The calorimetric data, therefore, give positive evidence of the existence of A2 for iron containing about 0.06 carbon.

From Meuthen's calorimetric observations, the amount of heat evolved at A2 is about the same as at A3, while by cooling curve methods all observers find the heat effect at A3 at least three times that at A2.

Critical ranges from heating and cooling curves.—An enormous amount of work has been done by thermal methods on the location of the critical ranges of steels and other ferrous alloys, much of which is very contradictory. This is discussed at length in several papers and especially in a recent one by Prof. H. M. Howe.[8] While some light may perhaps be thrown on the position and properties of A3 for pure iron from an examination of the behavior of impure irons, for the A2 transformation in pure iron, we would expect to learn little or nothing from a study of impure iron, on account of the very small quantity of heat involved in the transformation, which one would expect to be considerably masked or attenuated by the impurities present. It appears to be a remarkable fact, however, that, generally speaking, whenever A2 is detected at all, it is always found at the same temperature, whatever the composition of the iron alloy. For example, the discussion by Prof. Howe would place the break at O in the line GOS, Fig. 3, at 769° C., which is exactly the temperature we find experimentally for A2 maximum in pure iron. In other words, the A2 line for the Fe–C system is horizontal, as shown by practically all existing data, and the A2 point viewed in this way would appear to have the characteristics of a Fe–C eutectoid with the possible important if not crucial exception, of which we do not appear as yet to have sufficient experimental proof, that the quantity of heat

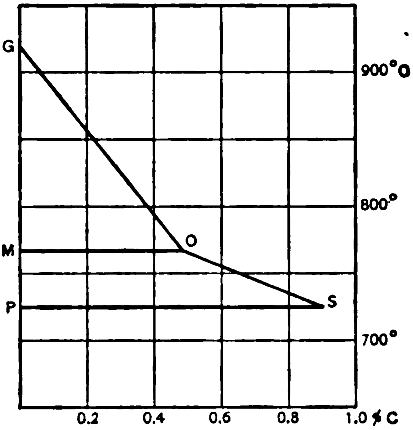

Fig. 3.—*Part of Fe–C diagram*

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[8] H. M. Howe: "Discussion of the existing data as to the position of Ac3," Trans. Am. Inst. Mining Engrs., 46, p. 1099; 1913.

involved in the A2 transformation does not vary appreciably with the carbon content from zero to 0.48 per cent. This constancy of heat of transformation, together with its constancy in temperature, if both be definitely proved by using a pure Fe–C system, lend force to the idea that A2 is a transformation independent of the carbon present, and from the work of Moore and others A2 appears to be independent in position also of metallic components.

As to A3, the comprehensive discussion by Prof. Howe leads to an equilibrium temperature Ae3 of 917° for pure iron. This temperature A3 = 917° also satisfies the observations of practically all recently published work with very pure iron.

Returning to the A2 range in pure iron and its location by heating and cooling curves, we are confronted by considerable contradictory evidence as to its existence, location, and type, whether possessing one or two cusps. Prof. Benedicks[4] discusses the evidence given by the thermal experiments of Osmond, Roberts-Austen, Arnold, and others and gives as well a consise critical summary of the whole subject of the nature of A2 in pure iron, as shown by experiment, and concludes that A2 is not an independent transition point but forms a part—a tailing off—of A3, which latter is taken as a transformation of Type IIa (see Fig. 1) and, "according to this, the nature of the β-iron is to be α-iron containing in solution a limited amount, increasing with temperature, of γ-iron."

Since Benedicks's publication we have the experiments of Carpenter, which he would have taken as verifying Benedicks's (or Smits's) theory; of Guillet and Portevin, who appear to find A2 and A3 as distinct transformations; and of Broniewski, whose results are ambiguous.

Let us consider the experiments of Carpenter more closely. His observations of 1904, taken in association with Mr. Keeling on iron containing 0.01 per cent carbon, showed Ar2 sharply defined at 762° and Ar3 at 900°. Carpenter's observations of 1913, using iron with 0.007 per cent carbon or of a carbon content hardly detectable in difference from his iron of 1904, also show

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[4] C. Benedicks: "On allotropy in general and that of iron in particular," Jl. Iron and Steel Inst., 86, p. 242; 1912.

Ar2 as present but not sharply defined and ranging from 768° to 741°, while Ac2 is not in general clearly defined by his curves except as a swell. The main differences in these two series appear to be that solid, rolled cylinders of iron five-eighths by five-eighths inch were used in the earlier, while in the later sheets of electrolytic iron 0.01 inch in thickness were rolled into a cylinder weighing 42 g. The curves differ in the main, as one would expect, the poorer conductivity and the presence of gases in the wound-up sheets of otherwise untreated electrolytic iron, producing a flattening out, distortion, and displacement of the critical regions, especially of the feebler A2. Similar remarks apply to the recent experiments of Honda, who used iron cylinders 3.25 cm long, and concludes that A2 is not sharply defined.

Several experimenters, notably Arnold, insist that A2 has a double cusp for pure iron, while it would appear from the work of several others, notably Carpenter and also Rosenhain, that A2 is erratic, sometimes showing a double and sometimes a single cusp.

Considering all the hitherto available data, there can be hardly any doubt that thermally there is a critical range for pure iron in the neighborhood of 770° (A2); but whether this be separate from the higher critical range near 900° (A3) and whether it (A2) be single or double cusped, the existing thermal observations do not prove conclusively, but a fair inference would be that A2 is single and independent of A3.

TABLE 1

Thermal Maxima of Critical Ranges of Pure Iron by Various Observers

Observer	Date	Carbon content, per cent	Iron content by difference	Ac2	Ar2	Ac3	Ar3	Remarks
Osmond	1887	....	....	....	750	......	890	Ar3 corrected from 855. Two maxima for Ar2.
Roberts-Austen	1891	0.007	....	....	(?)	......	895	
Arnold	1894	.003	99.967	740	740	860	854	Ar2 is double.
Charpy	1895	.007	....	740	730	865	840	
		.009	....	744	731	903	860	
Charpy and Grent	1903	tr.	....	775	730	935	900	
		.05	....	755	730	885	860	
Osmond	1899	Electrolytic Fe	....	800	780	905	880	
Carpenter and Keeling.	1904	.01	99.803	....	762	......	900	
Harkhort	1907	....	99.89	691 to 763	764 to 759	910 to 917	888 to 875	
A. Müller	1909	.017	99.803	770	763	917	894	23 observations in vacuo, all agreeing very closely.
Rosenhain and Humfrey.	1909	.029	99.66	770	763	941	904	
E. Colver-Glauert	1910	Fe "Kahlbaum."	....	....	....	......	......	A2 is double.
H. C. H. Carpenter	1913	.008	99.967	(?)	768 to 741	902 to 938	898 to 886	Ac2 not detected; 2 samples of same analysis; 10 observations.
Guillet and Portevin	1913	Not detected.	99.96	791	778	937	902	As deposited } Electrolytic.
				788	778	932	902	Annealed
Honda	1913	Fe "Kahlbaum."	....	795	787	933	915	A2 not sharp.

Summary of previous determinations of A3 and A2 in pure iron.—Without for the moment considering any theory concerning the meaning of the transformations in pure iron, let us consider what is the present experimental basis for the existence of A2 and A3, either as separate or associated transformations.

A summary of most of the experiments that have been made is given in Tables 1 and 2; the former includes only heating and cooling curve methods and the latter all others. These tables, taken in connection with the preceding paragraphs, show that there is overwhelming evidence for a discontinuity in properties of pure iron for the intervals of temperatures roughly defined as 700° to 780° and 850° to 950°, or corresponding to the critical ranges A2 and A3. (See also Fig. 2.)

TABLE 2

Critical Ranges in Pure Iron by Other than Cooling Curve Methods

Observer	Date	Carbon content per cent	Iron content by difference	A2	A3	Method and remarks
P. Curie	1895	0.04	99.9+	750	920	Magnetic
Morris	1897	0.006	99.925	765	....	Electrical resistance
		0.010	....	770 to 780	....	Magnetic
Hopkinson	1889	0.006	99.515	(?)	880	Electrical resistance
		0.010	99.128	775	....	Magnetic, cusp μ vs. T curve
Le Chatelier	1890	....	....	780	....	Electrical resistance
	1899	0.057	99.763	(?)	840	Expansion
Osmond	1900	Electrolytic		(?)	Detected	Crystallographic
Harrison	1902	(?)	(?)	Uncertain	....	Thermoelectric Cu-Fe couples, H atmos.
				760?	....	Electrical resistance
Belloc	1903	(?)	"Pure iron"	(?)	(?)	Thermoelectric
Charpy and Grenet	1903	0.03	....	....	860 to 890	Expansion
Boudouard	1903	? Commercial		775	885	Electrical resistance
Weiss and Beck	1908	(?)		760	....	Calorimetric; A3 not measured
Rosenhain and Humfrey	1909	0.029	99.767	Detected	Detected	Tensile and crystallographic, qualitative only
	1913	0.106	99.374	750	910	Tensile strength
Terry	1910	0.012	99.30	785	910	Magnetic
Somerville	1910	0.012	"Iron"	750	(?)	Electrical resistance
A. R. Meyer	1911	0.00	99.976	700	(?)	Fe "Kahlbaum" } Electrical resistance, cusp of dR/dt curve
		(?)	99.94	700	(?)	Ingot Iron
		0.00	99.85	705	(?)	Electrolytic
Weiss and Foëx	1911	Electrolytic		774	....	Magnetic; A3 not measured
Meuthen	1912	0.06	99.960	780	890	Calorimetric
Broniewski	1913	0.07	99.87	730	850	Thermoelectric
		Electrolytic		....	950 (^{a})	(^{a}) by Fe-Cu,
				730 (^{a})	1020 (^{b})	(^{b}) by Fe-Pt couple
				750 to 850	950 and 1020	Electrical resistance
				700?	890 to 950	Expansion
Stead and Carpenter	1913	0.007	99.967	Not detected	Detected	Crystallographic
Schneider et Cie	1913	0.060	99.378	770	....	Magnetic
Honda	1913	"Kahlbaum"		785	....	Magnetic

The existence of A3 is not open to question, it having been readily located by practically all methods of physical analysis, with the possible exception of electric resistance and thermoelectricity for which any discontinuity is not well defined. The magnetic change is also small, but abrupt and unmistakable. The thermal observations, which give the sharpest definition of A3, show that the maximum of Ar3 is always lower in temperature than that of Ac3.

Controversy has raged for a quarter century not only about the nature and extent but as to the very existence of A2, which has, however, been generally identified with the loss of ferromagnetism in iron. The point of inflection of the electrical resistance curve appears to be associated with the A2 region, as well as an abrupt change in specific heat of the same magnitude as at A3. The thermoelectric effect appears not less uncertain than at A3; there is a small but an abrupt change in tensile strength at A2; and there is a small thermal effect on heating and cooling which appears to remain at a constant temperature for the addition of carbon or metallic components in considerable quantities. Apparently the only phenomenon studied, which has hitherto always given negative results for A2, is crystalline structure.

Most, although not all, of the phenomena appear to indicate that A2 differs fron A3, in that for the latter the transformation is abrupt, taking place at a higher temperature with ascending temperature than with descending, while for the former, the transformation is more gradual (of Type II *a*, Fig. 1), but has the same location of maximum on heating and cooling. That A2 and A3 are parts of a single transformation, A2 being subordinated to A3, is a conclusion to be drawn with some difficulty from the data, and as pointed out by Guertler it is difficult to construct any plausible physicochemical theory which would admit of a distinct heat evolution at A2 and still have A2 a part of the A3 transformation, for "the end point is never marked by a sudden evolution of a new and constant thermal effect at a given temperature."

THE PRESENT INVESTIGATION

The object of the present investigation is to determine, with several samples of pure iron of different sizes, prepared by various methods, the exact location and nature of the A2 and A3 ranges, using the most refined methods of thermal analysis and keeping the samples free from the masking influences of occluded gases.

Experimental Method.—Two methods of taking heating and cooling curves have been used simultaneously on the same sample; one, the inverse-rate method of Osmond in which the times required for the specimen to rise or fall successive, equal temperature intervals are noted in terms of the temperature or ($dt/d\theta$ vs θ); the other, the derived differential method of Rosenhain, in which the observations are taken by the differential method of Roberts-Austen, using a "neutral" of platinum,[5] and in which for equal decrements or increments of temperature the difference in temperature between specimen and neutral is taken in terms of the temperature of the specimen ($\theta-\theta'$ vs θ) for $\Delta\theta=\text{const.}$ The results so obtained by the differential method are transformed into the derived differential curve by the operation of dividing the differences $\theta-\theta'$ for each temperature interval $\Delta\theta$ by this interval and plotting in terms of θ, or giving:

$$\frac{d(\theta-\theta')}{d\theta} vs\ \theta$$

These two methods of thermal analysis supplement each other most excellently as each is subject to different disturbing effects; and although obtained by totally different operations, the resulting heating or cooling curves are strictly similar, except for certain minor details which we shall mention later. To operate both methods simultaneously requires no more apparatus or observers than the differential method alone, although in this latter case the chronograph may, less conveniently, be replaced by any sufficiently exact timepiece. It is preferable to have two observers, although this is not essential.

The inverse-rate method is subject to error, due to drafts, sudden changes in current feeding the furnace, or any cause which may impress upon the specimen thermal changes not proper to it. Inversion of $dt/d\theta$ at recalescence, or an actual increase of temperature on cooling, is not readily expressible by other than a horizontal line in the plot; this weakness of analysis is of minor import, however, as the data on which the inverse-rate curve is based give, nevertheless, very sharply the beginning, maximum, end, and also, when present, the elevation in temperature accompanying a transformation. This last effect, of course, only accompanies a violent evolution of heat and is of no interest here.

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[5] For a detailed description of the methods of taking cooling curves, see G. K. Burgess, Reprint 99, Bull. Bur. Standards, 1909.

The derived differential method is less subject to error due to extraneous influences; recalescence can not be any more readily expressed by this method of plotting than the other. The presence and properties of a neutral free from transition ranges, as is platinum, have no appreciable effect on the location of the critical points of a substance such as iron.

Arrangement of the Apparatus.—The general appearance and arrangement of the apparatus is shown in Plate I, and a schematic diagram, Fig. 4, gives the layout of connections.

Measurement of Temperature.—For this purpose thermocouples were used connected to a five-dial, low-resistance potentiometer designed to be free from thermal electromotive forces, of the Diesselhorst type as constructed by Otto Wolff.

The moving coil galvanometer (from Leeds & Northrup) used with the potentiometer had a constant sensibility for all parts of the range of the potentiometer as used, and gave when critically damped a deflection of 25 mm on scale and telescope at 2 meters for each 20 microvolts of emf of the thermocouple. As used, it had a resistance of 57 ohms and a period of two seconds. This sensibility, which was ample, could have been increased if necessary. The zero shift was not troublesome and the instrument was glass inclosed, reducing temperature inequalities. The method of operation, whether for calibration, inverse rate, or differential curves, was to note times, preferably on the chronograph, and this invariably, when taking inverse-rate curves, every time the zero of the scale passed the cross hair of the telescope; the dial of the potentiometer was then turned, say, two steps, corresponding to about 2°, throwing the zero of the scale back about 25 mm, and the operation repeated indefinitely. The sensibility is about 0.01° with the Pt, Pt–Rh thermocouples.

Measurement of Time.—For recording the time measurements necessary for the inverse-rate method and convenient with the calibration of the couples and with the differential methods use was made of a cylindrical, motor-driven Geneva chronograph together with a telegraph key which, when depressed, gave a dash

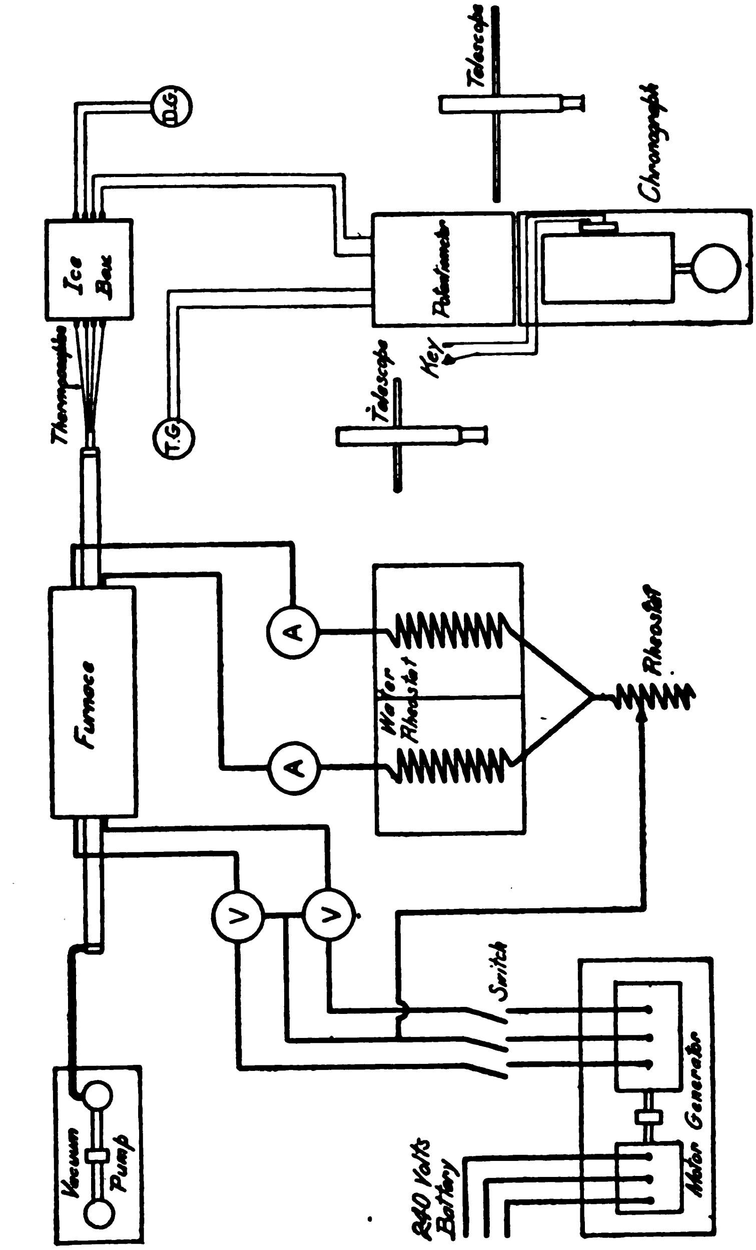

D.G.
Telescope
Chronograph
Ice Box
Potentiometer
Thermocouples
T.G.
Key
Telescope
Furnace
A
A
Water Rheostat
Rheostat
V
V
Switch
Vacuum Pump
240 Volts Battery
Motor Generator

Fig. 4.—Diagram of apparatus

on the chronograph sheet easily distinguishable from the seconds marked on the same sheet with the same pen when actuated through a relay by a standard clock situated in a distant constant-temperature room. The time observations were easily obtained to 0.1 second.

Thermocouples.—In some of the preliminary work various thermocouples of 0.6 mm diameter were used, but the later more reliable measurements were all taken with three Heraeus 0.4 mm × 150 cm thermocouples of platinum, 90 platinum–10 rhodium, marked M_1, M_2, and M_3, and all cut off the same batch of wire. These couples were frequently interchanged during the investigation. A differential thermocouple, M_4, for measuring the difference in temperature between the iron sample and the platinum neutral, was made by fusing a length of 45 mm of 90 Pt–10 Ir wire between two lengths of platinum wire of the same grade as in the temperature-measuring couples. The cold junctions of all thermocouples were always kept at 0° in a suitable ice box. (See Fig. 4.)

Temperature Scale and Calibration of Thermocouples.—The temperature scale used is that defined by the freezing points of the following pure metals:

	°C
Zinc	419.3
Antimony	630.0
Silver	960.0
Copper	1083.0

The calibration of the thermocouples was carried out as follows: The metals were melted in crucibles 14 cm deep of Acheson graphite of about 300 cc capacity in an Heraeus electric resistance furnace wound with platinum foil. The thermocouples while immersed in the metal were protected by out-glazed Berlin porcelain tubes of about 5 mm diameter. Both freezing and melting points were taken several times for a first calibration, and the couples were occasionally checked at the silver point during the progress of the investigation and recalibrated at the close, when they showed no appreciable change. All (M_1, M_2, M_3) satisfied the same equation between 400° and 1100° C, namely,

$$\underset{t_0=0}{\mathrm{emf}} = -313.8 + 8.259t + 0.001666t^2$$

where emf is expressed in microvolts and *t* is temperature centigrade. All thermocouple wires were electrically annealed at about 1400° C before using.

It is interesting to note the excellent behavior of these thermocouples in direct contact with iron. The fact that there was practically no oxidation of the iron together with the fact that the metals were always in a vacuum of the order of 0.01 mm Hg probably accounts for this constancy.

Mounting of Thermocouples.—One junction of the differential couple together with the hot junction of the temperature measuring couple were inserted in the iron specimen under observation and the other differential junction, which was about 4.5 cm away, was inclosed within the neutral, a platinum cylinder weighing 98 g. The bare wires were in direct contact with the iron, and in fact when very small samples were used, as the 0.7-g sample of iron from Prof. Carpenter, the iron was hammered onto the couples. The sketch, Fig. 5, gives an idea of the arrangement when small cylinders (10 to 30 g) were used.

Differential Measurements.—The differential couple was connected directly to a Siemens & Halske moving coil galvanometer of 200 ohms resistance. Deflections were read by means of a telescope and scale 2.5 m distant. As connected, the galvanometer gave a deflection of 60 mm for 100 microvolts, corresponding to a sensitiveness of nearly 0.01°

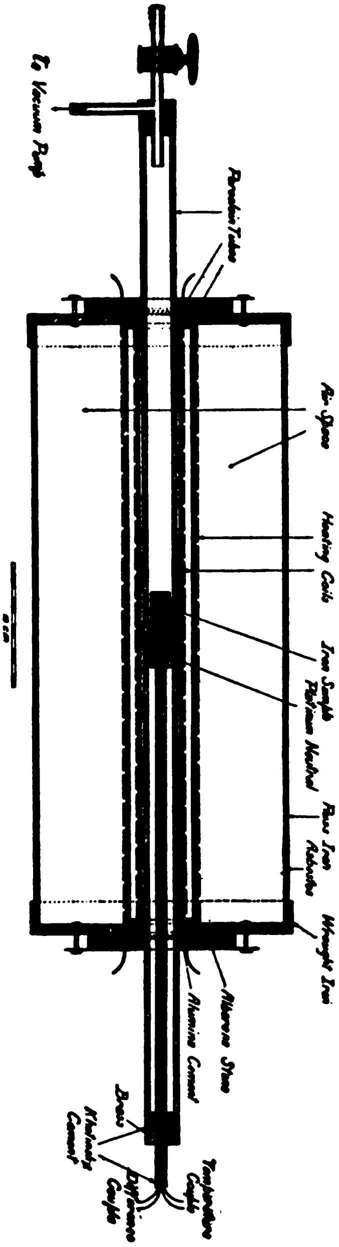

To Vacuum Pump
Porcelain Tubes
Air Space
Heating Coils
Iron Sample
Platinum Neutral
Pure Iron
Asbestos
Wrought Iron
Alundum Stem
Alundum Cement
Brass
Khotinsky Cement
Differential Couple
Temperature Couple

Fig. 5.—Furnace

with the Pt-Ir couple used. This was ample, and there would have been no advantage in increasing this sensitiveness, as could easily have been done fourfold by changing the galvanometer connections.

Furnace and Accessories.—The furnace, shown in Fig. 5, was constructed in the laboratory and consists essentially of four concentric tubes, three of Berlin porcelain and an outer one of iron backed with a one-eighth inch layer of asbestos. The innermost tube, which carries the specimens under study, is glazed both inside and out, so as to hold a vacuum, and extends beyond the furnace to receive seals of hard wax and metal for pump and thermocouple. There was no trouble in holding a vacuum of 0.01 mm Hg up to a temperature of 1050°. The two unglazed porcelain tubes each carry a separate heating coil of platinum foil 2 cm wide by 0.001 cm thick. In some of the preliminary work a furnace was used in which a single heating coil was wound directly on the glazed tube carrying the specimen. This earlier arrangement is less satisfactory than the one above described since the tube deteriorates sooner, and the uniformity of temperature is less well maintained. As will be noted, the furnace is provided with no other insulation than these concentric tubes, thus permitting, when desired, the use of faster rates of cooling and reaching more conveniently lower temperatures than when the furnace is packed with insulating material.

With the construction described there was no trouble whatever from drafts. The furnace was tested for freedom from critical ranges by taking several blank series of heating and cooling curve observations, using the usual platinum neutral and replacing the iron specimen with a cylinder of palladium. Some of these blanks are shown in Plate VIII.

The vacuum pump used is a two-cylinder motor-driven Geryk pump kept in condition to maintain a vacuum of 0.01 mm Hg in the furnace as measured with a mercury gauge and provided with drying tubes of phosphorus pentoxide.

The energy supply for heating the furnace was furnished by a 5-kw Siemens-Schuckert motor-generator set delivering alternating current to the furnace and operated on a 240-volt storage battery circuit. Two of the three phases generated by the alternator were used at a voltage which could be set anywhere between

50 and 170 volts. This somewhat elaborate arrangement was found to be highly desirable, when, as here, one is seeking minute thermal effects and every extraneous cause of variation in the rate of heating or cooling of the sample must be eliminated. There are two further advantages gained by using alternating current instead of direct for heating the furnace; it permits use of a liquid rheostat without polarization or electrolysis, and it eliminates any magnetic field about the iron sample. This last, if present, might conceivably influence the magnetic transformation in iron.

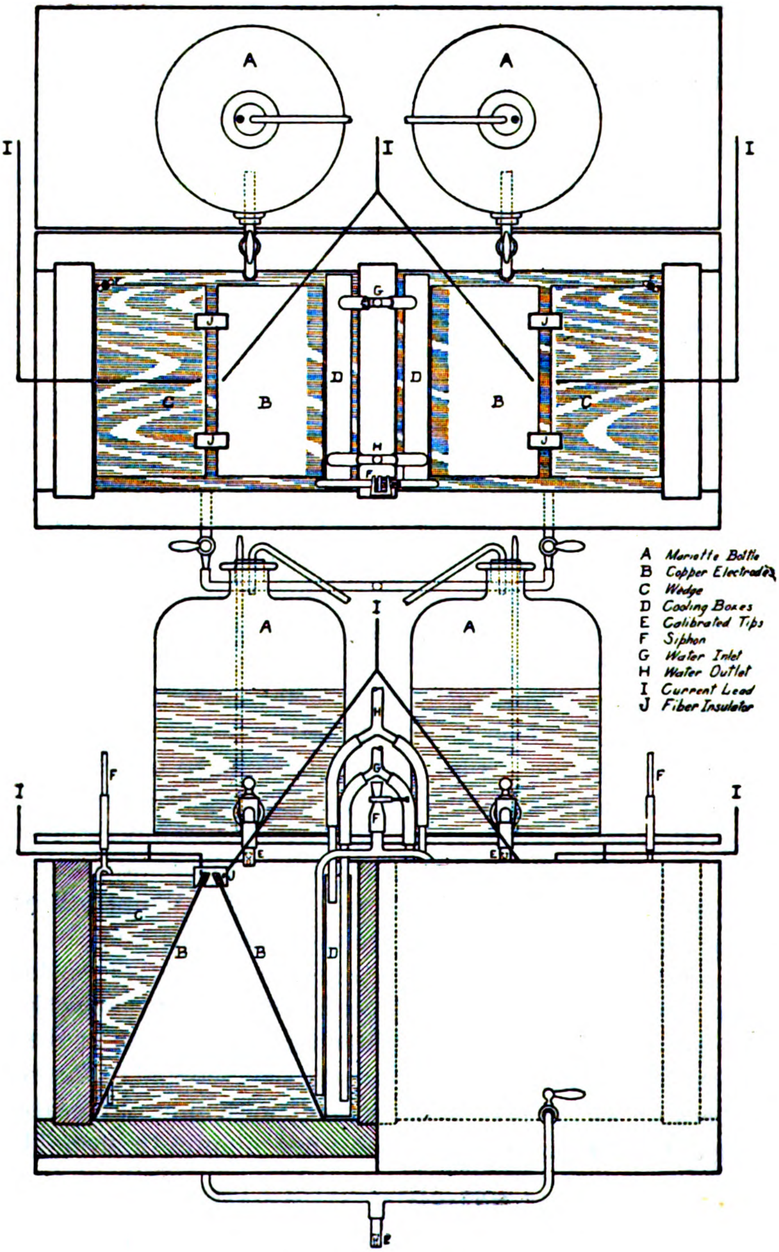
The rheostat, Fig. 6, deserves special mention, as it was specially designed to give automatically a constant rate of heating and cooling, variable at will within wide limits. In addition to the salt-water rheostat, wire rheostats were placed in the heating circuit.

It consisted of a cypress box of two compartments, each measuring 30 cm by 35 cm by 35 cm, in each of which were two copper plates (35 cm by 26 cm), placed 30 cm apart at the bottom and 1 cm apart at the top. A metal box through which cold water was circulated for the purpose of keeping the salt water cool was placed on each side of the partition. The outside copper plate in each compartment besides performing its functions as an electrode also formed one side of a wedge which opened at the top and could be filled with water before starting a run. This was done to cause the water which was fed at a constant rate from a Mariotte bottle to rise between the copper plates at a faster rate as the temperature of the furnace increased, thus overcoming the greater radiation losses to which the furnace is subjected at the higher temperatures and thereby giving a very constant rate over the whole range.

When taking cooling curves the water in the wedges was kept at the same level as the water in the compartment by connecting the two with a siphon; thus all the water was siphoned off at the same rate. A series of brass outlets were constructed and calibrated for this rheostat which gave a series of definite times of heating or cooling of the furnace, ranging from a few minutes to several hours.

THE MATERIALS INVESTIGATED

Sources of Iron.—It was considered worth while to examine the thermal behavior of several samples of pure iron prepared by different methods and subjected to various preliminary treatments.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A Mariotte Bottle
B Copper Electrodes
C Wedge
D Cooling Boxes
E Calibrated Tips
F Siphon
G Water Inlet
H Water Outlet
I Current Lead
J Fiber Insulator

Fig. 6.—*Rheostat*

We are indebted to Prof. C. F. Burgess, of Wisconsin, who furnished three samples of his electrolytic iron in the form of cathode plates together with an analysis; to Messrs. H. Goldschmidt and Cuntz, who furnished electrode plates and an analysis of iron obtained from the German firm of Langheim-Pfanhauser; to Prof. H. C. H. Carpenter, of Manchester, England, who kindly sent us some of the electrolytic iron he had used in his experiments on the critical ranges in pure iron, and which had been analyzed by Prof. J. E. Stead. Several samples of electrolytic iron were also prepared for this investigation at the Bureau of Standards by Messrs. Cain and Cleaves using a method which is to be described elsewhere. There is also included a sample of "ingot iron" for which we are indebted to the American Rolling Mill Co., of Middletown, Ohio.

Preparation and Description of Samples.—The samples were prepared for taking heating and cooling curves by cleaning with alcohol and ether. In the case of the untreated electrolytic irons of C. F. Burgess and Langheim-Pfanhauser the samples 1, 16, 17, and 26a, in the form of plates one-eighth to one-fourth inch thick, were bored out to receive the thermocouples. Some preliminary but less satisfactory measurements were made with small pieces packed about the thermocouples and within a thin-walled platinum cylinder of 3.5 cm length and 1.5 cm diameter. With this last arrangement the transition points were not always very sharply defined, due apparently to a progression of the reaction from one piece to another.

The first and often several of the succeeding curves taken with untreated electrolytic plates which are known to be heavily charged with gas, especially hydrogen, was erratic, an effect due for the most part to the presence of these gases within the sample, producing parasitic evolutions and absorptions of heat. (See Pl. XI.) This gas effect has been noticed by other observers.

To obviate this troublesome effect it was decided to melt some of the samples of iron before taking the heating and cooling curves, which melting was carried out successfully both in a vacuum electric furnace and in gas-fed furnaces. This melting of iron, provided contamination from crucible or furnace atmosphere is avoided, has the great advantage of further purifying the iron by the removal of all or nearly all of the contained gases. Electrolytic iron, for example, bubbles very violently on first melting in vacuo, showing that a considerable quantity of gas remains occluded to the temperature of fusion and is only removed by melting the iron. Melting in vacuo, as is shown for samples 25 and 26, as compared with 1 and 26a, Table 3, appears also to lower the already very small carbon content of the iron to almost nothing, again increasing the purity with respect to the most undesirable element, carbon. Finally, electrolytic iron, which has been melted either in vacuo or in gas furnaces, possesses a sharply defined heating curve the first time such iron is reheated, so that a very troublesome source of uncertainty is removed by this melting. That the presence of gases in the iron has a considerable effect on the location and range of the critical ranges is also shown in later paragraphs.

For all these reasons it appeared to us desirable, when making a thermal study of iron and its alloys which occlude or contain gases, to remove these gases by a previous melting of the metal, preferably in vacuo.

There was considerable range in mass (0.7 to 35 g) from one sample to another used in taking heating and cooling curves, as is shown in Tables 4 and 6. It is our experience that it is advantageous to work with as small samples as the precision of the experimental method will permit when it is desired to locate the exact temperatures of the critical ranges of the material. The apparent advantage to be gained with larger samples, which absorb or set free greater quantities of heat, appears to be more than offset by the conductivity of the larger sample not being sufficient to transmit promptly enough the heat generated to the thermometric device. If there is nonuniformity of temperature throughout the sample, this effect is enhanced, and a phenomenon which really takes place at a single temperature will then appear to be spread over a range of temperatures.

We believe this spreading and attenuation of the reaction is a principal reason why Prof. Carpenter was not able to detect Ac2 with certainty when using 42 g of metal in the form of a thin sheet coiled into a cylinder, while with only 0.7 g of his iron we were able to locate Ac2 with great sharpness. (See Pl. VI.)

For melting in vacuo the Arsem furnace was used, the iron being contained in a crucible of pure magnesia placed within a tube of Marquardt porcelain. For melting in the gas furnace covered clay crucibles brasqued with pure fused magnesia were used.

Chemical analyses.—The chemical analyses of the different preparations of iron used are shown in Table 3, including mention of who furnished the analyses. Those at the Bureau of Standards were made by Messrs. Cain, Cleaves, Tucker, and Witmer. In all cases the analyses were made of the metal in the condition stated in the column headed "Description," and the pieces for analysis were cut from the cylinder or plate used for taking the heating and cooling curves. It will be noted that the purest iron is 99.983 Fe, obtained by remelting electrolytic iron in vacuo in magnesia crucibles. The two samples remelted in vacuo are also the lowest in carbon content, 0.003 and 0.001 per cent, respectively. The average carbon content of all samples is 0.009 and the range 0.001 to 0.015. It is of interest to note that with the exception of the Mn and Cu contents, the "ingot iron" is nearly as pure as the average of the electrolytic irons.

Where there are check analyses by different chemists, and in the case of the carbon determinations by different methods, when one considers the difficulty of exact determination of such small quantities of impurity, the agreement is extremely satisfactory, and in most cases may well be within the degree of homogeneity of the samples. None of the samples was analyzed for oxides, but their amount, if present, must be very small.

TABLE 3

Description and Chemical Analyses of Pure Iron

Source	Description	Analysis furnished by—	No.	C	S	P	Si	Mn	Cu	Fe by difference
H. C. H. Carpenter.	Electrolytic 0.01-inch sheet.	Stead	F5	0.008	Tr.	0.002	0.014	0.009	......	99.967
American Rolling Mill Co.	"Ingot iron" remelted in gas furnace.	Bureau of Standards.	F1	.012	0.020	.001	.003	.029	0.03	99.905
J. R. Cain	Electrolytic remelted in gas furnace.	do	F2	.008	.045	Tr.	.004	Tr.	<.001	99.941
				.009	.045	......	......	......	......	......
Langheim - Pfanhauser.	do	do	F3	.007	.011	<.001	.004	Tr.	......	99.977
C. F. Burgess	do	do	F4	.009	.010	......	......	......	......	......
					.009	<.001	.006	Tr.	.006	99.968
J. R. Cain	do	do	F6	.019	<.001	Tr.	.007	Tr.	<.001	99.975
				.013	......	......	......	......	......	......
				[6].015	......	......	......	......	......	......
Do	do	do	F7	[7].014	<.001	Tr.	.003	Tr.	<.001	99.971
C. F. Burgess	Electrolytic remelted in vacuo.	do	25	.003	.006	.004	.004	.000	......	99.983
Langheim - Pfanhauser.	do	do	26	.001	.004	.006	.007	.000	......	99.982
Do	Electrolytic plates.	do	26a	.008	.004	<.001	.006	Tr.	.011	99.970
		H. Goldschmidt.		.00	.00	.007	.00	.00	.008	99.98
C. F. Burgess	do	Bureau of Standards.	1	.009	.003	<.001	.006	Tr.	.006	99.975
		C. F. Burgess		.012	.00	.004	.013	.00	......	99.971

[6] By solution.

[7] First burning, 0.008 C; second burning, 0.006 C.

EXPERIMENTAL DATA

We have divided the data into two chronological portions:

1. A preliminary series of observations carried out with a furnace and rheostat of somewhat less satisfactory form than that of Figs. 5 and 6, with less precautions for holding a good vacuum and steady current, and in part with the iron samples in a less concentrated form; nor was the thermocouple calibration as carefully checked in all cases. These preliminary observations, although we do not place the reliance on all of them, for the exact

location of temperatures that we do on the definite series, are, nevertheless, quite instructive in showing some of the things that should be avoided in the exact thermal analysis of a substance occluding gases, and also furnish data for discussing the effects of varying some of the factors that influence the location of the critical ranges.

2. The definite series of observations were then carried out with all the precautions and improvements in method and manipulation our preliminary measurements had shown to be necessary; it is on this definite series, together with the last two of the preliminary series, that we mainly base our conclusions regarding the allotropy of iron as shown by thermal analysis.

In all cases, attention should be given mainly to the location of the maxima of the critical ranges, as the beginnings and endings, especially the former, on heating are, in general, not to be located with exactness.

Preliminary observations have already been reported on briefly, but are here included in full for the sake of completeness. (See Table 4.) The numerical values here given are in some cases slightly different from those previously published, due to some of the indications of one of the thermocouples needing correction. Three Pt–Rh. thermocouples, C_1, W_{11}, and W_{14}, were used in these preliminary observations.

All but one of the samples of iron are electrolytic. Three from Prof. C. F. Burgess, Nos. 1, 16, and 17; sample No. 25 remelted in vacuo is from the same lot as No. 17; and No. 26 is from the Langheim-Pfanhauser A–G. iron, also remelted in vacuo. The electrolytic plates were relatively thick, from one-eighth to nearly one-fourth inch.

The mass of the samples ranged from 15 to 31g, and for the first three series the iron sample consisted of more than one piece of metal. The first three, 1, 16, and 17, were from the electrolyte plates as deposited, 25 and 26 were remelted in vacuo, and 22 is ingot iron remelted in a gas furnace, of similar quality as sample F1 of Table 3.

TABLE 4

Preliminary Series of Observations

Date	Couple	Sample No.	Mass in g	Rate—Degs/Secs		Beginning						Maximum						End					
				Up	Down	Ac2	Ar2	Ac2–Ar2	Ac3	Ar3	Ac3–Ar3	Ac2	Ar2	Ac2–Ar2	Ac3	Ar3	Ac3–Ar3	Ac2	Ar2	Ac2–Ar2	Ac3	Ar3	Ac3–Ar3
1911																							
July 25	W11	1	15	0.194	0.138	......	......	......	894	904	−10	785	768	+17	944	896	+48	......	......	......	957	879	+78
26	W11	1	15	.254	.224	......	776	......	915	899	+16	812	754	58	936	896	40	829	724	+105	957	872	+85
27	W11	1	15	.100	.189	766	773	− 1	906	903	+03	772	758	14	922	895	27	798	723	+ 75	935	879	+56
28	W11	1	15	.255	.308	769	......	......	901	901	00	788	754	34	933	892	41	814	......	......	943	867	76
Mean	......	......	......	......	......	768	774	− 2	904	902	+ 2	789	758	+31	934	895	+39	814	724	+ 90	948	874	+74
Nov. 8	W14	16	15	......	.150	......	776	......	......	902	......	......	754	......	......	893	......	......	711	......	......	883	......
8	W14	16	15	.349	.284	770	761	+ 09	885	915	−30	796	739	+57	901	887	+14	813	714	+99	908	863	+45
9	W14	16	15	.083	.063	717	888	−171	902	904	− 2	773	766	7	918	898	20	785	......	......	926	888	38
11	W14	16	15	.118	.132	779	779	0	902	902	0	782	761	21	918	897	21	791	......	......	939	880	50
11	W14	16	15	.284	.221	773	761	+ 12	915	907	+ 8	791	755	36	930	892	38	817	......	......	944	878	66
13	W14	16	15	.069	.088	763	776	− 13	904	901	+ 3	769	764	5	916	898	18	789	......	......	924	889	35
Mean	......	......	......	......	......	760	790	− 52	902	905	− 4	782	757	+25	917	894	+22	799	712	+99	926	880	+48
Nov. 21	W14	17	20	.104	.124	......	......	......	......	896	......	767	756	+11	911	890	+21	......	......	......	925	863	+62
21	W14	17	20	.192	.196	709	767	− 58	......	894	......	773	763	10	915	887	28	......	......	......	935	......	......
23	W14	17	20	.057	.061	......	......	......	......	897	......	770	767	3	913	893	20	775	......	......	921	......	......
27	W14	17	20	.140	.157	751	......	......	......	897	......	771	761	10	915	889	26	775	......	......	923	865	58
Dec. 4	W14	17	20	.055	.065	......	......	......	......	897	......	......	765	......	......	893	......	......	......	......	......	875	......
Mean	......	......	......	......	......	730	767	− 58	......	896	......	770	762	+8	913	890	+24	775	......	......	926	868	+60

1912																							
Feb. 16	W14	22	29	.118	.127	......	784	......	875	902	−27	768	772	−04	908	890	+18	782	742	+ 40	925	875	+50
19	W14	22	29	.150	.124	737	......	......	893	895	−02	768	772	−04	913	887	26	784	......	......	926	873	53
19	W14	22	29	.319	.256	746	784	− 38	893	893	00	768	772	−04	913	881	32	793	......	......	937	866	71
21	W14	22	29	.160	.202	756	794	− 38	893	896	−03	768	772	−04	913	887	26	784	......	......	926	862	64
23	W14	22	29	.175	.153	......	784	......	893	902	−09	768	772	−04	913	887	26	788	......	......	928	866	62
26	W14	22	29	.137	.148	756	784	− 28	893	893	00	769	772	−03	913	885	28	784	751	+ 33	928	866	62
1913																							
Mar. 5	W14	22	29	.066	.062	746	784	− 38	893	902	−09	768	772	−04	913	892	21	782	756	+ 26	924	878	46
12	W14	22	29	.167	.156	746	784	− 38	875	895	−20	772	771	+01	917	887	30	......	......	......	932	866	66
Mean	......	......	......	......	......	748	785	− 36	888	897	−09	769	772	−03	913	887	+26	785	750	+ 33	928	869	+59
1912																							
July 19	W14	25	31	.121	.181	......	773	......	909	905	+ 4	769	769	0	918	900	+18	781	733	+ 48	931	887	+44
22	W14	25	31	.070	.063	728	778	− 50	913	905	8	768	768	0	914	03	11	774	751	23	928	893	35
22	W14	25	31	.247	.289	......	809	......	913	904	9	768	768	0	918	00	18	779	747	32	929	884	45
29	W14	25	31	.132	.155	......	821	......	911	905	6	768	768	0	913	00	13	779	742	37	931	886	45
Aug. 5	W14	25	31	.066	.079	......	772	......	911	906	5	768	769	− 1	913	02	11	775	761	14	924	894	30
6	W14	25	31	.094	.051	......	773	......	911	907	4	768	769	− 1	......	04	......	775	761	14	......	893	......
Oct. 22	C1	25	31	.078	.126	......	777	......	909	906	3	769	770	− 1	915	04	11	775	......	......	929	894	35
Mean	......	......	......	......	......	728	787	− 50	911	905	+ 6	768	769	0	915	902	14	777	749	28	929	890	+48
Aug. 14	W14	26	21	.217	.248	......	773	......	907	909	− 2	768	768	0	911	904	+ 7	779	......	......	929	893	+36
15	W14	26	21	.209	.192	......	826	......	913	909	+ 4	765	768	− 3	918	904	14	779	733	+ 46	930	891	39
16	W14	26	21	.096	.142	......	835	......	912	910	+ 2	768	767	+ 1	915	905	10	773	737	36	926	895	31
16	W14	26	21	.082	.095	......	......	......	913	909	+ 4	766	......	......	915	906	9	......	......	......	925	897	28
21	W14	26	21	.099	.153	......	826	......	912	910	+ 2	767	768	− 1	915	907	8	774	742	32	925	895	30
28	W14	26	21	.063	.054	......	907	......	913	912	+ 1	768	768	0	915	908	7	775	747	28	925	899	26
29	W14	26	21	.248	.275	......	819	......	913	913	0	764	768	− 4	918	904	14	......	......	......	928	891	37
Mean	......	......	......	......	......	......	831	......	912	910	+2	767	768	− 1	915	905	10	776	740	+36	927	894	+32

Several facts stand out prominently from these preliminary observations. In the first place, in contrast to the samples remelted in vacuo, before taking heating and cooling curves, which samples show the Ac2 and Ar2 maxima sharply defined at a single temperature, 768°, the untreated electrolytic samples show a wide and variable interval between the Ac2 and Ar2 maxima, an interval in some individual cases greater than 50°. With untreated electrolytic iron, Ac2 is always higher and Ar2 always lower than the single A2 point at 768°, as found with the remelted irons. Again, the position of the maxima of Ac3 is higher and of Ar3 lower, with very considerable variations for the untreated samples; or, in other words, the interval Ac3–Ar3 (maxima) is considerably less, 10 to 14°, for the samples reheated in vacuo than for the untreated samples, for which this interval ranges from 20 to 40°.

These results show the important rôle played by the occluded gases and an examination of the data of the tables shows that several reheatings to 1050° in vacuo are not sufficient to put thick electrolytic iron plates into a satisfactory condition for making a thermal analysis of its critical ranges. When there are several pieces making up a sample (as Nos. 16 and 17) the retarding effect of poor conduction also enters somewhat.

Remelting appears from these observations to be an essential preliminary treatment to which the iron should be subjected, unless several rates are used, as we shall show below. We desire to emphasize this point, for we believe that one of the main reasons why many of the previously published results with electrolytic iron show inconsistencies and variations in the location of A2 and A3, is due to the fact that the gases have never been sufficiently removed or the samples were not in a compact enough form, or both these effects superposed and sometimes associated with a too wide temperature interval between observations.

A property that appears to be common to all these samples is that, on the average, for A3 the beginning of Ac3 is at the same temperature as the beginning of Ar3, within the limit of accuracy with which these somewhat indefinitely defined temperatures can be located. This characteristic sharply distinguishes A3 from

A2; for the latter, as we have seen, the maxima of Ar2 and Ac2 coincide when the samples are compact and gas free.

As to the effect of rate of heating or cooling upon the location of the critical ranges, it will be noted, Table 4, that for the rates here used, 0.06° to 0.35° per second (or 17 to 3 seconds per degree), there is no effect on the location of A2 (max) for the samples 25 and 26 premelted in vacuo, or for sample 22, ingot iron remelted in gas furnace, while for the untreated samples a fast rate accompanies a greater difference in Ac2–Ar2. For the A3 range the effect of rate is less pronounced for the untreated samples but appears to be appreciable for the premelted samples. Table 5 shows that reducing the rate to zero gives 769° for A2 (= Ac2 = Ar2) for all samples; and for A3 we find for zero rate Ac3 – Ar3 = 12° with Ac3 = 912° and Ar3 = 900° on the average.

TABLE 5

Maxima of Critical Ranges for Zero Rate—Preliminary Series

Sample	Ac3	Ar3	Ac3-Ar3	Ac2	Ar2	Ac2-Ar2
1	914	900	14	768	767	+1
16	913	900	13	769	769	0
17	911	896	15	770	769	+1
22	909	895	14	769	772	−3
25	912	903	9	769	769	0
26	913	909	4	768	768	0
Mean	912	900	12	769	769	0

It therefore appears that in spite of the wide variations noted in Table 4, the nature of the sample, whether or not gas free or whether in one or several pieces, does not influence the location of the maxima of the critical ranges when reduced to zero rate of heating and cooling.

The definite series of observations is shown in Table 6, in which are recorded all the observations taken with the improved apparatus of Figs. 4, 5, and 6 on the samples here included. There are three samples of electrolytic iron, prepared by Messrs. Cain, Cleaves, and Schramm (F2, F2′, F7); an electrolytic sample (F3), prepared by Langheim-Pfanhauser; another (F4), from Prof. C. F.

Burgess; and one of ingot iron (F1), from the American Rolling Mill Co., all of which were remelted in a gas furnace before taking observations. In addition, F8 and F9 are small samples from Nos. 25 and 26, respectively, of the preliminary series; and F5 is a piece from an electrolytic sample which had been studied thermally by Prof. Carpenter.

Considering first the existence and location of the maxima of the A2 range, the observations on all these nine samples show most emphatically the existence of a common maximum for Ac2 and Ar2 at 768°, with agreement of 1° among the samples. This result is identical with that found in the preliminary series for the samples Nos. 25 and 26, reheated in vacuo, and for the others of this series when reduced to zero rate. This constancy of (maximum of) Ac2 = Ar2 = 768° C ±0.5 is seen, therefore, to persist for variations in mass from 0.7 to 35 g. in rate of heating or cooling from 0.05° to 0.35° per second, for iron remelted in vacuo or gas furnace, whether of electrolytic or "ingot" preparation, as determined in two differently constructed furnaces, with five separately calibrated thermocouples and using two methods of thermal analysis.

TABLE 6

Definite Series of Observations

Date	Couple	Sample No.	Mass in g	Rate—Degs/Secs		Run No.	Beginning						Maximum						End					
				Up	Down		Ac2	Ar2	Ac2–Ar2	Ac3	Ar3	Ac3–Ar3	Ac2	Ar2	Ac2–Ar2	Ac3	Ar3	Ac3–Ar3	Ac2	Ar2	Ac2–Ar2	Ac3	Ar3	Ac3–Ar3
1913																								
May 19.......	M1	F2	33	0.143	0.155	1	......	776	......	868	891	−23	767	765	+2	911	876	+35	774	736	38	923	849	+74
20.......	M1	F2	33	.101	.131	2	748	776	−28	858	891	−33	769	767	2	912	879	33	774	739	35	922	858	64
27.......	M1	F2	33	.121	.093	3	......	808	......	874	892	−18	768	767	1	912	882	30	775	729	46	922	......	......
27.......	M1	F2	33	.138	.128	4	......	808	......	876	889	−13	768	768	0	912	880	32	775	736	39	923	858	65
28.......	M1	F2	33	.053	.063	5	......	808	......	893	893	00	768	768	0	912	883	29	772	748	24	919	863	56
29.......	M1	F2	33	.075	.083	6	......	779	......	......	894	......	768	768	0	912	881	31	773	744	29	922	858	64
June 5.......	M1	F2	33	.102	.092	7	......	819	......	......	......	......	768	768	0	......	......	......	775	741	34	......	......	......
5.......	M1	F2	33	.115	.078	8	......	775	......	......	......	......	768	768	0	......	......	......	775	......	......	......	......	......
5.......	M1	F2	33	.131	.222	9	......	......	......	......	......	......	768	767	1	......	......	......	774	......	......	......	......	......
7.......	M1	F2	33	.088	.100	10	755	......	......	......	891	......	768	......	......	911	880	31	773	......	......	920	855	65
				.068	.107	10	......	790	......	892	889	−03	......	767	......	910	879	31	......	......	......	919	858	61
14.......	M1	F2′	1.5	.128	.090	1	......	804	......	......	888	......	768	768	0	910	880	30	772	767	05	921	849	72
Mean.......	......	......	......	......	......	......	752	794	......	877	891	−15	768	767	+1	911	880	+31	774	742	+51	921	856	+65
June 11.......	M1	F3	32	.130	.125	1	......	776	......	891	891	00	768	768	0	914	880	+34	776	......	......	920	858	62
11.......	M1	F3	32	.151	.143	2	......	776	......	890	890	00	768	768	0	914	882	32	776	......	......	922	863	59
12.......	M1	F3	32	.053	.064	3	......	775	......	858	894	−36	768	768	0	911	886	25	771	......	......	920	880	40
Mean.......	......	......	......	......	......	......	......	776	......	880	892	−12	768	768	0	913	883	+30	774	......	......	921	867	+54

TABLE 6—Continued

Definite Series of Observations—Continued

Date	Couple.	Sample No.	Mass in g	Rate—Degs/Sec		Run No.	Beginning						Maximum						End					
				Up	Down		Ac2	Ar2	Ac2-Ar2	Ac3	Ar3	Ac3-Ar3	Ac2	Ar2	Ac2-Ar2	Ac3	Arc	Ac3-Ar3	Ac2	Ar2	Ac2-Ar2	Ac3	Ar3	Ac3-Ar3
1913																								
July 8	M1	F4	37	.164	.144	1	762	775	−13	894	894	0	768	768	0	916	886	+30	776	743	+33	925	868	+57
10	M1	F4	37	.051	.062	2	751	771	−20	885	897	−12	768	769	−1	912	890	22	771	753	18	921	879	42
14	M1	F4	37	.136	.081	3	759	773	−14	897	895	+ 2	768	768	0	914	890	24	776	750	16	920	877	43
Mean							757	773	−16	892	895	− 3	768	768	0	914	889	+25	774	749	+22	922	875	+47
July 17	M2	F5	0.7	.131	.107	[8] 1	......	769	......	911	904	+07	768	766	+2	912	888	+24	772	753	+19	921	893	+28
17	M2	F5	0.7	.057	.054	2	......	769	......	912	903	09	767	766	1	910	889	21	771	756	15	920	895	25
Mean							......	769	......	912	904	+08	768	766	+1	911	888	+23	772	754	+17	920	894	+26
July 31	M2	F7	13	.147	.125	1	......	776	......	876	892	−16	768	766	+2	912	888	+24	774	748	+26	916	876	40
31	M2	F7	13	.103	.105	2	......	774	......	872	895	−23	768	766	2	910	889	21	773	......	......	919	872	47
Mean							......	775	......	874	894	−20	768	766	+2	911	888	+23	774	748	......	918	874	+44
July 23	M1	F1	35	.177	.112	1	......	785	......	880	894	−14	768	766	+2	916	884	+32	774	748	+ 26	925	858	+67
24	M1	F1	35	.057	.043	2	......	785	......	867	896	−29	768	768	0	911	889	22	772	748	24	920	867	53
Mean							......	785	......	874	895	−21	768	767	+1	914	886	+28	773	738	+25	922	862	+60
Aug. 11	M2	[9] F8	1.0	.064	.095	1	......	785	......	907	901	+06	768	766	+2	913	898	+15	773	......	......	921	890	+31
13	M2	[10] F9	2.1	.099	.101	1	......	786	......	912	905	+07	768	766	+2	916	903	+13	774	......	......	925	897	28

[8] By Bureau of Standards.

[9] Piece of No. 25 which has been run.

[10] Piece of No. 26 which has been run.

The small electrolytic sample, F5, from Prof. Carpenter, which had been heated by him six times to 1000° C, also behaves exactly like the others.

Turning now to the maxima of A3 we see that for all the samples, Ac3 is located at 912° ± 2, while the agreement for Ar3 is apparently not so good, the range being from 880° to 903° for the different samples, and the mean value of Ar3 is 889°. It is to be noted that the samples F8 and F9, preheated in vacuo, are in agreement with Nos. 25 and 26 of the preliminary series, again showing the smallest interval, namely, $Ac3 - Ar3 = 14°$.

As in the preliminary series, the beginning of Ar3 is located, in general, at about the same temperature as the beginning of Ac3, although these beginning temperatures are not defined with sufficient sharpness to warrant certainly the statement that the A3 transformation begins at the same temperature on heating and on cooling, although this appears highly probable.

No effect of rate of heating or cooling can be seen in the location of the critical range A2. For the critical range A3, when the observations on Ac3 and Ar3 are plotted in terms of rate of heating or cooling (see Fig. 7), the anomalies in location of Ar3 largely disappear, although extrapolating Ac3 and Ar3 to zero rate again fails to give a single equilibrium temperature Ae3. For zero rate, $Ac3 = 909°$ and $Ar3 = 897°$, or there is apparently a real difference of some 12° in the location of the maxima of this transformation, which result is in exact agreement with the preliminary series.

Considering both series, it seems safe to say that we may place $Ac3 = 909° \pm 1$ and $Ar3 = 898 \pm 2$ and $Ac2 = Ar2 = 768° \pm 0.5$ for pure iron passing through A3 and A2 at zero rate and through A2 at any rate provided the iron is gas free and in the form of a single compact piece.

DESCRIPTION OF THE PLOTTED CURVES

An examination of the actual heating and cooling curves is also essential. For most of the samples both inverse rate (marked I) and derived differential (marked D) heating and cooling curves are recorded. Observations were usually taken at 2° intervals, although others were sometimes used, namely, 1° and 4° steps,

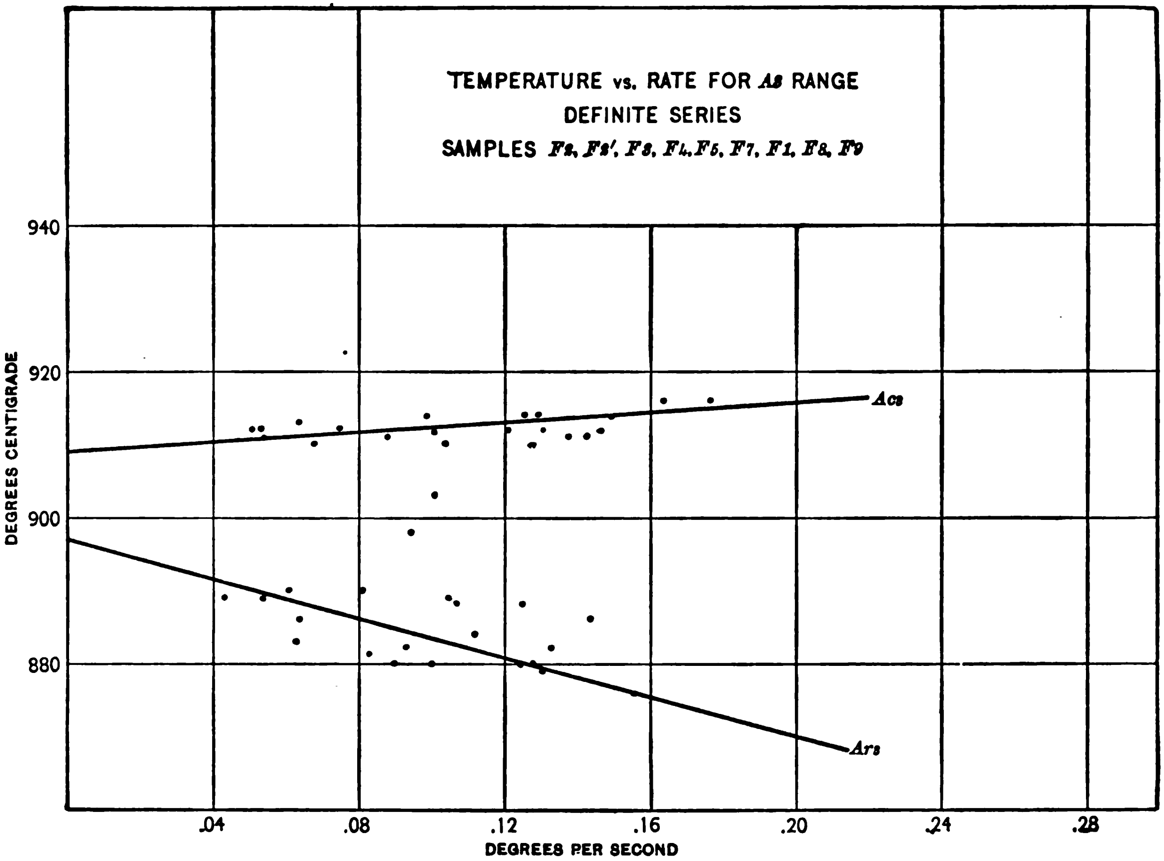

Fig. 7.—*Temperature vs. rate for A3 maxima*

which are evident from inspection. For all curves the ordinates represent temperatures centigrade; for the inverse rate curves the abscissas represent time in seconds to change the temperature of the sample by the unit interval (1°, 2°, or 4°); and for the derived differential curves the abscissas represent deflections on the differential galvanometer scale expressed in millimeters.

Effect of plotting at different intervals is shown in Plate III for the observations of a single heating and cooling curve of sample F1. It would appear that there is no advantage in reducing the interval at which temperatures are taken to as small as 1° in the desire not to miss any very slight transformation; on the contrary, the sensibility is thereby reduced proportionally, since what is measured is only the effect between two successive taps of the key. On the other hand, with wide intervals, such as 4°, missing a single observation may be sufficient to throw the whole series into doubt. The interval chosen, 2°, appears to avoid, satisfactorily, the two pitfalls of lack of sensibility and danger of missing the cusp of a transformation.

Curves of the definite series are shown in Plates IV to VIII. The most detailed study was made of sample F2, consisting of 33 g of premelted electrolytic iron, prepared by Mr. Cain. In contrast to the observations by ourselves and others on untreated electrolytic iron which show irregular curves for the first three or four heatings, with this premelted iron the first curve is about as regular and sharply defined as the succeeding ones. The similar character of the two types of curve is well shown here, the only considerable difference being that for very slow and for rapidly changing rates the inverse-rate curve shows marked departures from the vertical. It is apparent from an inspection of the curves that although the maxima and to a less degree the ends of the critical ranges are sharply defined, the exact location of the beginnings, especially on heating, is attended with considerable uncertainty for both types of curve.

The curves of Plate IVa show the results of an effort to attenuate or eliminate, if possible, by various operations, the A2 point. As the curves indicate, it is impossible to influence the position or nature of Ac2 or Ar2 by any thermal operations performed upon the iron above or below this temperature. Thus, during the sixth heating the sample was held 71 minutes at 825°, then heated to above A3 and then cooled; in the seventh it was heated to just below the beginning of A3 and then cooled; in the eighth and ninth it was heated and cooled twice over a short range including the A2 point; in the tenth it was held 60 minutes just below A3 and then carried up and down three times over the A3 range before cooling. In all these operations, Ac2 and Ar2 remain unchanged in any way, and the evidence is abundantly conclusive that the critical range A2 is in no sense related to the A3 transformation, as has been suggested it might be, particularly by Benedicks.

A small piece (1.5 g = F2′) of the above sample was also examined with the same results (Pl. IV).

The observations, with several other samples of electrolytic iron, F3, F4, and F7 premelted in the gas furnace, are shown in Plates V, VII, and VIII, corroborating the previous observations. It will be seen that in each case the first heating gives as definite results as the succeeding ones. A sample of 35 g of remelted ingot iron F1 (Pl. VII) gives the same type of curve as the remelted electrolytic irons.

A sample of particular interest is F5, it being 0.7 of a gram of Prof. Carpenter's electrolytic iron, which is seen (Pl. VI) to behave exactly like the others, showing Ac2 and Ar2 both clearly located on the curves at 768°.

The advantage of using small samples for sharply defining the magnitude of the critical ranges is well shown for the curves of F5 (0.7 g), F8 (1.0 g), and F9 (2.1 g), Plates VI and VII, the last two being pieces remelted in vacuo. These very small samples were also inclosed within the platinum neutral in the furnace, a proceeding which appears to be advantageous, since the sample F2′ of 1.5 g not so inclosed (Pl. IV) shows the A3 range much less sharply.

The curves of the preliminary series are not all presented here, but a sufficient number are included to indicate the constancy of behavior attained with the variously prepared samples with the imperfected apparatus and at times an unsteady heating current. All the observations taken of one of the electrolytic samples premelted in vacuo (No. 26) are given and this series of curves (Pls.

X, Xa, and Xb) gives a fair example of them all. Some of the untreated electrolytic samples give somewhat erratic results, as shown for sample No. 1, Plate XI. The curves for the ingot iron, sample No. 22, Plates IX and IXa, are also representative of the results obtained with the earlier apparatus. Plate XI is interesting mainly in that it contains about all the errors to which thermal analysis is subject. This was our first series for pure iron.

Existence of Other Critical Ranges.—Several observers have announced the existence of transformation points in addition to A2 and A3; notably, Sir Roberts-Austen, who considered he had found several points below A2; Carpenter, one at 600°, which Rosenhain later attributed to the heating tube; Arnold a "fourth recallescence point" between A3 and A2 (or a doubling of A2); Robin, two critical regions below A2 near 400° and 100°, respectively; and P. Curie, Broniewski and others, one or more points above 1000°.

A few of our observations extend to as low as 300° and as high as 1050° without indicating the presence of any critical regions above A3 or below A2.

Some of the curves, particularly on cooling, give slight evidence of a minute transformation at about 805° (see in particular several of the cooling curves for sample F2), although with the other samples this point can hardly be said to be present. If a point between A3 and A2 is really present, this would corroborate the magnetic observations both of Curie and of Weiss and Foex, whose susceptibility curves show an inflection between A2 and A3. (See Fig. 2.)

There is more positive evidence of a slight absorption of heat in the heating curves corresponding in temperature to the maximum of Ar3. Although not always present in the heating curves, this doubling of Ac3 is well shown, mainly for the inverse-rate curves, in the following of the definite series: Sample F7, both curves; the curves of very slow rate of sample F2, especially the fifth; F4, all curves; F3, F1, and F8, slightly evident; while this doubling is apparently absent in F9 and F5 (Carpenter's sample), both of very small mass.

Some of the curves of the preliminary series also show one or another of these secondary points (see Pls. IXa and Xb), usually more marked in the inverse-rate curves; but due to the relative irregularity of the preliminary series, as compared with the definite series with the perfected apparatus, we do not place any considerable reliance on the former series for this purpose.

In view of the apparent impossibility of finding experimentally a common equilibrium temperature Ae3 for the heating and cooling curves, the presence of an inferior, even if slight, transformation on heating at the temperature of Ar3 would be an aid in explaining this anomaly, although the allotropy of iron would thereby be further complicated, a step we are by no means anxious to champion, unless the facts are considered sufficiently convincing.

ILLUSTRATIVE SERIES OF OBSERVATIONS

In Table 7 are given the actual observations taken for our heating and cooling curves of sample F3, showing the method of recording and reducing such observations. These observations are plotted in Plate XII both as differential and derived differential curves. The abscissas of the differential curves are millimeter deflections on the galvanometer scale, as given by the differential thermocouple. It is evident from inspection why the derived differential method is to be preferred over the differential as a method of expressing graphically the results of thermal analysis.

The inverse rate curves deduced from Table 7 are given in Plate VIII.

In Table 7, the column headed "M1" gives emfs of thermocouple M1 measuring the temperature of the sample F3; the one headed "Time," the intervals in seconds as obtained from the chronograph sheet for M1 to change 20 micro volts; "M4," the corresponding deflection in millimeters of the galvanometer measuring the difference in temperature between sample and neutral; and "dt" the successive differences of M4.

TABLE 7

Sample No. F3. Run first up. Observers, J. J. C. and H. S. Couples$\left\{\begin{matrix}\mathrm{dt} & \mathrm{M4} \\ \mathrm{T} & \mathrm{M1}\end{matrix}\right\}$. Maximum temperature, 1005°. Date, June 11, 1913. Pot. Wolff. E. M. F. S. & S. Machine on battery. Time: Beginning, 10.49; ending, 11.42; total time, 53 minutes. Remarks: Weight of sample, 31.7 g; length of sample, 25 mm; diameter of sample, 15 mm. Hole, 17 mm deep; 5 mm diameter.]

M1	Time	M4	dt	M1	Time	M4	dt	M1	Timo	M4	dt	M1	Time	M4	dt
500		684		546		640		592		587		638		466	
	18.6		00		15.5		+01		14.3		+04		13.6		+07
02		684		48		639		94		583		40		459	
	19.0		+01		15.5		+02		14.1		+01		13.5		+05
04		683		50		637		96		582		42		454	
	18.3		+01		15.4		00		14.3		+03		13.7		+08
06		682		52		637		98		579		44		446	
	18.3		+02		15.4		00		14.2		+06		13.8		+08
08		680		54		637		600		573		46		438	
	18.1		+02		15.1		+04		13.9		+05		13.5		+08
10		678		56		636		02		568		48		430	
	18.1		+03		15.2		+03		14.0		+05		13.6		+07
12		675		58		633		04		563		50		423	
	18.1		+03		15.3		+01		14.1		+05		13.7		+09
14		672		60		632		06		558		52		414	
	17.8		+02		14.9		+02		13.9		+04		13.7		+09
16		670		62		630		08		554		54		405	
	17.8		+03		14.9		+01		13.9		+05		13.6		+09
18		667		64		629		10		549		56		396	
	17.6		+04		15.0		+02		14.0		+05		13.6		+08
20		663		66		627		12		544		58		388	
	17.9		+06		14.8		+02		13.8		+07		13.7		+10
22		657		68		625		614		537		60		378	
	17.8		+08		14.7		+01		14.0		+04		13.5		+08
24		649		70		624		16		533		62		370	
	17.4		+05		14.7		+01		13.9		+06		13.8		+10
26		644		72		623		18		527		64		360	
	17.0		+01		14.8		+03		13.8		+04		13.6		+09
28		643		74		620		20		523		66		351	
	16.4		00		14.5		+04		13.7		+07		13.6		+10
30		643		576		616		22		516		68		341	
	16.6		+01		14.7		+04		13.9		+04		13.7		+11
32		642		78		612		24		512		70		330	
	16.3		+01		14.5		+04		13.7		+06		13.5		+11
34		641		80		608		26		506		72		319	
	16.2		+01		14.6		+03		13.9		+07		14.0		+11
36		640		82		605		28		499		74		308	
	16.2		00		14.5		+03		13.5		+06		13.8		+12
538		640		84		602		30		493		76		296	
	15.8		00		14.3		+02		13.7		+07		13.9		+11
40		640		86		600		32		486		78		285	
	15.9		00		14.4		+04		13.5		+06		13.8		+12
42		640		88		596		34		480		80		273	
	15.9		+01		14.3		+05		13.8		+07		14.0		+12
44		639		90		591		36		473		82		261	
	15.7		−01		14.3		+04		13.7		+07		14.0		+16

TABLE 7—Continued

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
684		245		734		300		784		544		834		532	
	14.0		+14		11.6		−14		12.2		−07		14.1		+06
86		231		36		314		86		551		36		526	
	13.8		+14		11.6		−12		12.5		−05		14.3		+06
88		217		38		326		88		556		38		520	
	14.1		+14		11.6		−14		12.4		−05		14.6		+08
90		203		40		340		90		561		40		512	
	14.1		+16		11.7		−12		12.6		−05		15.0		+10
92		187		42		352		92		566		42		502	
	14.3		+16		11.5		−13		12.4		−05		15.1		+11
94		171		44		365		94		571		44		491	
	14.6		+19		11.6		−12		12.6		−04		14.8		+11
96		152		46		377		96		575		46		480	
	14.6		+19		11.8		−11		12.7		−04		15.0		+14
98		133		48		388		98		579		48		466	
	14.7		+25		11.7		−10		12.8		−04		15.3		+16
700		108		50		398		800		583		50		450	
	15.0		+26		11.8		−11		12.9		−01		15.5		+19
02		82		52		409		02		584		52		431	
	13.7		+04		11.7		−11		13.0		−01		15.8		+22
04		78		54		420		04		585		54		409	
	12.2		−10		11.9		−10		13.1		+01		16.4		+29
06		88		56		430		06		584		56		380	
	11.9		−13		12.0		−10		13.2		+01		17.0		+34
08		101		58		440		08		583		58		346	
	11.9		−14		11.8		−10		13.3		+01		17.5		+40
10		115		60		450		10		582		60		306	
	11.6		−18		11.9		−10		13.6		+02		18.8		+49
12		133		62		460		12		580		62		257	
	11.5		−14		11.9		−09		13.7		+04		19.8		+59
14		147		64		469		14		576		64		198	
	11.5		−17		12.1		−08		13.4		+03		18.2		+34
16		164		66		477		16		573		66		164	
	11.5		−16		12.1		−08		13.7		+04		13.4		−30
18		180		68		485		18		569		68		194	
	11.4		−15		12.0		−09		13.9		+06		10.2		−56
20		195		70		494		20		563		70		250	
	11.6		−16		12.2		−09		13.7		+03		9.4		−58
22		211		72		503		22		560		72		308	
	12.0		−15		12.1		−07		13.8		+06		9.4		−55
24		226		74		510		24		554		74		363	
	10.9		−16		12.3		−07		14.1		+04		9.8		−49
26		242		76		517		26		550		76		412	
	11.4		−15		12.1		−07		13.8		+04		10.0		−42
28		257		78		524		28		546		78		454	
	11.5		−14		12.2		−08		14.0		+04		10.5		−39
30		271		80		532		30		542		80		493	
	11.6		−15		12.2		−06		13.8		+05		11.0		−31
32		286		82		538		32		537		82		524	
	11.5		−14		12.5		−06		14.1		+05		11.2		−30

TABLE 7—Continued

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
784		554		902		697		920		734		938		732	
	11.5		−24		13.2		−07		14.7		−01		15.6		+01
86		578		04		704		22		735		40		731	
	11.6		−24		13.7		−06		14.6		−01		15.2		+01
88		602		06		710		24		736		42		730	
	12.2		−20		13.6		−06		14.6		+01		15.2		+01
90		622		08		716		26		735		44		729	
	12.3		−16		13.7		−04		15.0		−01		15.6		+03
92		638		10		720		28		736		46		726	
	12.5		−16		14.0		−04		14.6		00		12.5		+02
94		654		12		724		30		736		48		724	
	12.7		−12		13.8		−03		15.1		+01		15.4		+01
96		666		14		727		32		735		50		723	
	13.0		−12		14.4		−03		15.0		+01				
98		678		16		730		34		734					
	13.1		−10		14.2		−02		14.9		+01				
900		688		18		732		36		733					
	13.3		−09		14.2		−02		15.1		+01				

[Sample No. F 3. Run first down. Observers, J. J. C. and H. S. Couples$\left\{\begin{matrix}\mathrm{dt\ M\,4}\\ \mathrm{T\ M\,1}\end{matrix}\right\}$ Maximum temperature 964. Date June 11, 1913. Pot., Wolff. E. M. F. S. & S. Machine on battery. Time: Beginning 1.32; ending, 2.27; total time, 55 minutes.]

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
950		175		930		97		908		53		886		30	
	26.5		−11		18.4		−06		16.2		−03		15.3		−02
48		164		28		91		06		50		84		28	
	24.5		−10		18.3		−05		16.1		−02		15.1		−03
46		154		26		86		04		48		82		25	
	24.3		−10		18.0		−04		16.3		−01		15.1		−01
44		144		24		82		02		47		80		24	
	22.2		−06		17.7		−04		15.8		−03		15.1		−01
42		138		22		78		900		44		78		23	
	21.8		−09		17.5		−04		15.9		−01		15.0		00
40		129		20		74		898		43		76		23	
	.....		−07		17.2		−05		15.8		−03		14.8		−02
38		......		18		69		96		40		74		21	
					17.0		−04		15.7		−02		14.8		−01
	2)40.8		−07	16		65		94		38		72		20	
	20.4				16.9		−02		15.5		−02		15.2		−01
36		115		914		63		92		36		70		19	
	19.9		−07		16.7		−03		15.6		−03		14.7		−01
34		108		12		60		90		33		68		18	
	19.3		−07		16.7		−04		15.3		−01		14.7		−01
32		101		10		56		88		32		66		17	
	18.7		−04		16.3		−03		15.3		−02		14.7		−02

TABLE 7—Continued

Mi	Time	M4	dt	Mi	Time	M4	dt	Mi	Time	M4	dt	Mi	Time	M4	dt
964		15		914		768		764		461		714		523	
	14.9		−01		13.5		− 07		13.3		−04		14.4		+09
62		14		12		761		62		457		12		532	
	14.6		−01		13.8		− 12		13.3		−03		14.2		+08
60		13		10		749		60		454		10		540	
	14.6		−01		13.2		− 15		13.3		−02		14.6		+12
58		12		08		734		58		452		08		552	
	14.5		−01		13.0		− 17		13.3		−02		14.7		+14
56		11		06		717		56		450		06		566	
	14.5		−01		12.7		− 18		13.4		−01		14.9		+16
54		10		04		699		54		449		04		582	
	14.7		−01		12.6		− 19		13.4		00		14.8		+24
52		09		02		680		52		449		02		606	
	14.4		−01		12.7		− 21		13.7		00		18.0		+41
50		08		800		659		50		449		700		647	
	14.6		00		12.4		−19		13.4		00		16.8		+35
48		08		798		640		48		449		698		682	
	14.3		−01		12.3		−18		13.4		+01		16.4		+25
46		07		96		622		46		450		96		707	
	14.5		00		12.4		−19		13.6		+01		15.6		+22
44		07		94		603		744		451		94		729	
	14.4		00		12.5		−16		13.9		+01		15.5		+17
42		7		92		587		42		452		92		746	
	14.3		00		12.6		−16		13.5		+03		15.0		+14
40		7		90		571		40		455		90		760	
	14.3		00		12.6		−14		13.5		+02		14.7		+11
38		7		88		557		38		457		688		771	
	14.5		+ 04		12.6		−14		13.8		+04		14.7		+10
36		11		86		543		36		461		86		781	
	14.9		+ 09		12.6		−11		13.7		+03		14.4		+07
34		20		84		532		34		464		84		788	
	15.7		+ 20		12.9		−11		14.0		+03		14.2		+06
32		40		82		521		32		467		82		794	
	17.2		+ 40		12.9		−11		13.6		+04		14.2		+03
30		80		80		510		30		471		80		797	
	20.9		+ 95		12.8		−10		13.9		+04		13.9		+04
28		175		78		500		28		475		78		801	
	32.4		+235		12.9		−07		13.8		+05		13.8		+03
26		410		76		493		26		480		76		804	
	34.8		+200		13.1		−08		14.0		+07		13.8		+02
24		610		74		485		24		487		74		806	
	24.4		+ 90		13.1		−07		13.9		+06		13.7		+01
22		700		72		478		22		493		72		807	
	19.5		+ 40		13.2		−05		14.0		+07		13.6		00
20		740		70		473		20		500		70		807	
	17.5		.....		13.0		−05		14.1		+07		13.7		−01
18		......		68		468		18		507		68		806	
	16.5		.....		13.0		−05		14.2		+08		13.4		−01
16		......		66		463		16		515		66		805	
	14.0		.....		13.5		−02		14.1		+08		13.4		−02

TABLE 7—Continued

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
664		803		622		732		580		654		538		600	
	13.5		−01		13.0		−02		13.0		−04		13.2		−04
62		802		20		730		78		650		36		596	
	13.2		−02		13.0		−05		13.0		−03		13.3		−03
60		800		18		725		576		647		34		593	
	13.3		−02		13.0		−03		12.9		−02		13.3		−03
58		798		16		722		74		645		32		590	
	13.3		−03		12.9		−04		13.3		−02		13.2		00
56		795		14		718		72		643		30		590	
	13.1		−02		13.1		−05		13.3		−02		13.3		−01
54		793		12		713		70		641		28		589	
	13.3		−03		12.8		−04		12.8		−02		13.5		−02
52		790		10		709		68		639		26		587	
	13.2		−04		12.9		−04		12.8		−03		13.2		−03
50		786		08		705		66		636		24		584	
	13.3		−03		13.0		−03		13.3		−03		13.3		−04
48		783		06		702		64		633		22		580	
	13.1		−03		13.0		−04		13.2		−03		13.5		−02
46		780		04		698		62		630		520		578	
	13.1		−04		13.0		−04		13.2		−04		13.3		−01
44		776		02		694		60		626		18		577	
	13.0		−03		13.0		−03		13.0		−03		13.3		−01
42		773		00		691		58		623		16		576	
	13.1		−05		12.9		−03		13.3		−03		13.4		−02
40		768		598		688		56		620		14		574	
	13.3		−03		13.0		−04		13.1		−03		13.5		+01
38		765		96		684		54		617		12		575	
	12.9		−04		13.2		−03		13.2		−02		13.7		−01
36		761		94		681		52		615		10		574	
	13.1		−04		12.8		−04		13.1		−02		13.4		−03
34		757		92		677		50		613		08		571	
	12.8		−05		13.1		−04		13.2		−02		13.5		−02
632		752		90		673		48		611		06		569	
	13.2		−04		12.9		−04		13.2		−04		13.8		−00
30		748		88		669		46		607		04		569	
	12.9		−03		13.2		−04		13.4		−01		13.4		−03
28		745		86		665		44		606		02		566	
	13.0		−04		13.1		−03		13.0		−03		13.8		−01
26		741		84		662		42		603		00		565	
	13.0		−05		13.1		−04		13.1		−02				
24		736		82		658		40		601					
	12.9		−04		13.0		−04		13.4		−01				

MICROSCOPICAL EXAMINATION

By H. S. Rawdon

Figs. 1 and 8 of Plates II and IIa, which are micrographs of a sample of electrolytic iron prepared by Mr. J. R. Cain, Bureau of Standards, illustrate the appearance of the metal upon deposition. The iron is quite different in its properties from iron under ordinary conditions. It is quite brittle and hard, and the samples for microscopic examination are prepared with much less difficulty than after the iron has been melted. This difference is undoubtedly due to the hydrogen which saturates the metal as a result of its method of preparation.

All of the other specimens examined show some spherical gas bubbles due to the liberation of the dissolved gases during the processes of melting and which did not escape from the iron on account of its viscosity. These bubbles have a peculiar appearance under vertical illumination, resembling inclusions of MnS. This is due to the absence of all oxide film from the walls of the bubble. Fig. 5 shows this appearance of the bubbles somewhat. These bubbles occur in all the specimens regardless of their method of melting, and also very small ones occur in samples which were heated for the cooling curve determination without previous melting. Fig. 3 is interesting in showing the interior veinings in the iron crystals which appear upon deep etching after the sample has been heated considerably.

All of the photomicrographs, unless otherwise stated, are at a magnification of 100 diameters. Picric acid was used as an etching agent.

SUMMARY AND CONCLUSIONS

In the first part of this paper, after a brief statement of the current theories of the allotropy of iron, we have given what we hope will be considered an impartial account of the numerous experimental efforts of others to locate and define the critical ranges A2 and A3 of pure iron in terms of the various physical phenomena which have been found to change with temperature.

These observations are embodied in Tables 1 and 2, from which we see that all the physical properties of iron which have been studied, with the single notable exception of crystallographic structure, have shown, in the hands of one or more skillful experimenters, a distinct discontinuity for the A2 range as well as for the A3 range. For several of the phenomena, such as electrical resistance, thermoelectricity, specific heat, and magnetism, it would appear that the discontinuity is at least as great for A2 as for A3, while the thermal effect has, of course, been long recognized as being much the more pronounced at A3.

The investigation proper consisted in taking in vacuo some 130 heating and cooling curves by two methods simultaneously, the inverse rate and differential, for 15 samples of pure iron prepared by various methods and analyzed by several chemists. Unusual precautions were taken to secure uniformity of heating of the samples, and it was also possible to take observations for samples of widely different mass, and over a wide range of rates each maintained strictly constant. Two furnaces were used and temperatures were taken with six separately calibrated thermocouples. The observations show that in order to get consistent and reliable results in the thermal analysis of a substance such as iron, the properties of which are so readily susceptible to many minor influences, it is necessary to get rid of all the disturbing influences.

We find essential the following precautions:

1. The iron should be pure—our purest samples were 99.983 and contained 0.003 per cent carbon or less—and it should be kept pure by heating it only in vacuo; a pressure of 0.01 mm Hg suffices.

2. Either the occluded gases should be removed by premelting the iron, preferably in vacuo, or it will in general be found necessary to take a series of heating and cooling curves at widely different rates, in order to determine correctly the location of the critical ranges A3 and A2.

3. The iron should be in a single piece, entirely surrounding and in contact with the thermocouple junction; otherwise the thermocouple will integrate the irregular progress of the heat through the sample and the curves will lose their sharpness. Small samples (1 g. or so) give sharper results than large samples.

4. The interval of recording temperatures should be wide enough that sufficient sensibility is attained and narrow enough

that the contour of the curves is not distorted; we have found a 2° interval satisfactory.

5. The sensibility of the apparatus indicating temperatures and differences of temperature should be of the order of 0.01° and time should be measured to better than 0.2 second.

Among the results of this investigation may be mentioned the demonstration that the inverse rate and differential methods, the latter plotted as the derived differential curve, give identical results of the same sensibility for the critical ranges, and the two sets of curves are strictly similar, save for minor particulars.

The plotted curves give what seems to us conclusive evidence of the independent existence of A3 and A2, all of the 130 curves, without exception, showing both these critical ranges sharply defined and unquestionably distinct. It was found impossible to eliminate or attenuate A2 by thermal treatment. The A2 transformation has not a double cusp, nor do there appear to be other transformations above A3 and below A2 between 300° and 1050°. With electrolytic iron, unless the sample has been premelted into a compact mass, erratic results will be obtained for both A3 and A2, the location of the critical points apparently depending in the main upon the rate of heating or cooling. The critical points may even be displaced by over 50°. (See Tables 4 and 6.) It is possible, however, to reduce the observations on untreated electrolytic iron to exactly the same temperature basis as the gas free, compact material by taking curves at several rates and reducing to zero rate. This would appear to indicate that the gases occluded, mainly hydrogen, play no essential chemical rôle in modifying the iron equilibrium.

Even with gas-free iron the A3 point is not entirely independent of the rate of heating or cooling, so that it is necessary to reduce the observations to zero rate in order to obtain correct results for Ac3 and Ar3. The range in the location of Ar3, for example, with premelted samples was found to be 876° at 0.155 degree seconds to 898° at zero rate. (See Fig. 7.)

All preparations of pure iron, even those containing gases, when reduced to the common basis of zero rate of heating or cooling, have the same maximum for the A2 critical range,[11] namely, A2 = Ac2 = Ar2 = 768° ± 0.5. All but one of the 15 samples gave this result to within 2°; the other to 3°.

Similarly for zero rate, the value of the maxima of A3 are found to be Ac3 = 909° ± 1 and Ar3 = 898° ± 2.

It was not possible to infer a single equilibrium temperature Ae3 from these experiments, the Ac3 transformation on heating always being at a higher temperature than Ar3, the transformation on cooling.

It was found, however, that the beginning of Ac3 coincides in temperature with the beginning of Ar3 as closely as could be judged. It is as if the crystallographic changes at A3 required, so to speak, a temperature inertia to complete itself both on heating and on cooling, although the effect of rate on the equilibrium (see Fig. 7) appears to be slightly the greater on cooling.

It is possible that the A3 transformation is somewhat more complex than this, as there are indications from some of the heating curves of a doubling of Ac3, although not of Ar3. This effect may be fortuitous.

The relative amounts of heat accompanying the two transformations, A3 and A2, is approximately 3 to 1, respectively.

An examination of some of the heating curves will perhaps give the erroneous impression that Ac2 is an evolution rather than an absorption of heat. The swing back at the maximum is very abrupt, following what appears to be a gradual building up of this maximum from an indeterminate low temperature. This behavior would be in accordance with the gradual change in certain physical properties, such as magnetism and electrical resistance, as A2 is approached. On the other hand, the opera-

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[11] Prof. Benedicks having raised the question of the effect on A2, due to an alternating current heating supply, the authors have taken heating and cooling curves of a sample in vacuo within an ordinary gas-heated muffle furnace, with the following results for A2 maxima:

Date	Sample	Rate—Degree seconds		Ac2	Ar2
		Up	Down		
1913.				°	°
Dec. 1	F7	0.08	0.33	766	768
Dec. 1	F7	.14	.24	768	770
Dec. 1	F7	.15	.05	768	768
Dec. 1	F7	.23	.23	768	770

tions carried out on sample F2 (Pl. V) failed to diminish sensibly the intensity of Ac2, which would imply that this thermal transformation is limited to a narrow temperature interval; also some of the curves of Ac3 show that this long back swing appears to be in part at least a property of the heating conditions. The shading off on cooling through Ar2, if this effect is a real one, might be marked by a similar swing back from this peak, and therefore be indistinguishable. (Compare also Plate XII.)

We hesitate to express an opinion on the nature of the allotropy of iron. These thermal observations appear to show that the transformations A3 and A2 are of the types illustrated in Fig. 8. The fact that A2 appears to be accompanied by no crystallographic change, such as accompanies A3, requiring a violent rearranging of relatively large crystal masses and involving a considerable quantity of heat, may account for the sharpness with which Ac2 equals Ar2, and the A2 transformation may be merely molecular, not involving the crystallographic structure as such. Whether we have any β iron or not to inhabit the region between A2 and A3

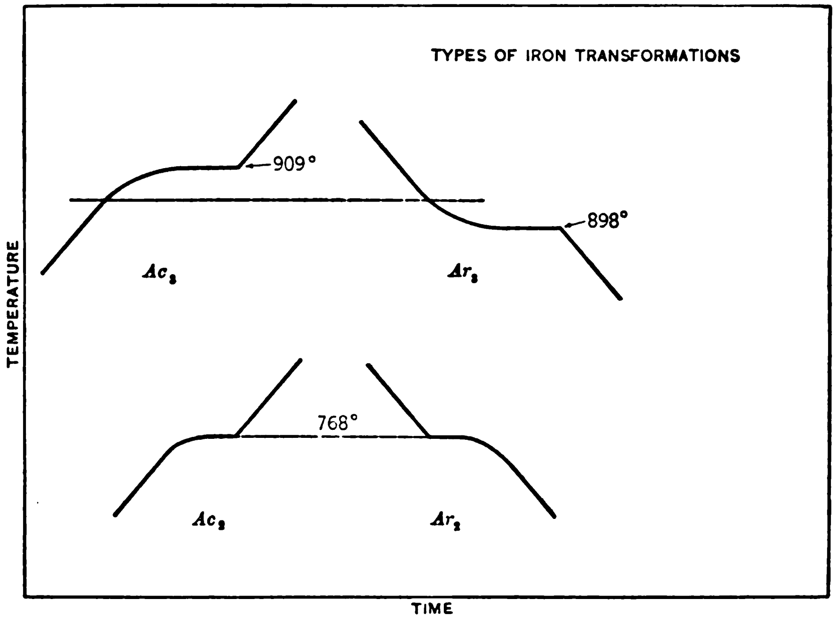

Fig. 8.—*Types of transformation in iron.*

will depend on our definition of allotropy, but we hope that we have proved beyond a reasonable doubt that under standard conditions there is a definite transformation at 768° and a less well defined although more intense one at 898° to 909° in terms of their maxima on cooling and heating.[12]

In conclusion, we take great pleasure in acknowledging the samples of iron and analyses from Prof. C. F. Burgess, Prof. H. C. H. Carpenter, Dr. H. Goldschmidt, Mr. J. R. Cain, and the American Rolling Mill Co., and the cooperation of the chemical division of this Bureau, in making check analyses. The care and skill with which Mr. H. Scott has assisted us in taking and reducing the observations has greatly expedited the investigation, and we are indebted to Mr. H. S. Rawdon for the photomicrographic examinations.

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[12] The authors would suggest the following concerning the theory of allotropy of iron:

1. Some of the experimental facts that any theory must satisfactorily account for are: A definite thermal effect, independent of rate of heating or cooling, located at 768°±0.5=Ac2=Ar2, i. e., with no measurable lag; a much greater thermal effect, but dependent upon rate, accompanying a marked crystallographic change, and, as extrapolated for zero rate, located at Ac3=909° and Ar3=898°. Both the Ac2 and Ac3 maxima appear to be anticipated by gradual changes in physical properties below these temperatures defining the maxima. Finally, A2 and A3 are distinct transformations.

2. Among the experimental uncertainties are, whether with A2 there is associated any crystallographic change, however slight—it being recalled that the thermal change is also very slight—and whether there is any slight volume change accompanying A2. Concerning A3, we are not sure whether, as zero mass and zero rate are approached, Ac3 exactly equals Ar3 or not. For neither A2 nor A3 has the beginning of Ac2 or Ac3 been exactly located.

3. We may define an allotropic transformation in many ways. Confining ourselves to a pure substance in the solid state, let us make the simple definition: *An allotropic transformation is one accompanied by crystallographic change.*

4. There appears to be no doubt that A3 is an allotropic transformation under this definition, whether or not for zero rate and mass Ac3=Ar3, so long as there is observed a crystallographic change. It is not necessary in the case of iron to add to the definition the complications of Smits's theory, actually observed with the masses hitherto used experimentally, namely, that Ac3>Ar3, and the faster the rate the greater the interval Ac3−Ar3.

5. Sufficient experimental evidence is yet wanting to decide in favor of A2 being an allotropic transformation according to the above definition.

6. So much for facts and theory. We still have the realms of analogy and hypothesis to work upon to guide us as to the probable nature of A2 in terms of allotropy. One of the greatest experimental difficulties encountered is due to the nontransparency of iron crystals rendering an adequate optical examination of iron passing through A2 well-nigh hopeless.

Turning to the transparent substance quartz, however, we have a material which appears to present a close analogy in certain of its transformations to those in iron. At 575°, quartz has a very minute transformation although a definitely defined one by thermal analysis, corresponding evidently to our A2 in iron. At about 900° there is a violent crystallographic change in quartz accompanied by a correspondingly large thermal effect and also by a very considerable volume change; in iron, exactly our A3. Now it is interesting to note that for the reversible point at 575° in the transparent quartz, there is a very slight crystallographic change accompanied by a minute volume effect which anticipates the sharp maximum at 575° by many degrees in the same way that the numerous physical properties of iron appear to anticipate the sharp maximum of iron at Ac2=768°.

7. Reasoning from the quartz analogy, therefore, the following hypotheses may be made regarding the nature of the A2 transformation in iron, namely, that A2 is an allotropic point accompanied by a very minute but as yet undetected crystallographic change and differing from A3 mainly in magnitude; that when sufficiently exact expansion measurements are made on pure iron, a minute but abrupt volume change will probably be found at A2 preceded by a very feeble anticipatory region in the expansion curve below A2.

If experiment eventually proves the first of the above hypotheses incorrect, we have the oft-expressed alternative that the A2 transformation is mainly if not entirely associated with the passage from the ferromagnetic to the paramagnetic state; and under the above definition, A2 would not be an allotropic transformation, and β iron would be really dead.

WASHINGTON, December 1, 1913.

WASHINGTON, September 22, 1913.

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This list of references to the literature of the critical points of pure iron makes no pretense of being complete. Many of the papers dealing mainly with the theoretical and controversial aspects of the subject are omitted, but it is believed that a sufficient number of titles concerning the experimental aspects of the subject are included to enable anyone to readily get in touch with the subject. The papers are grouped in terms of the principal phenomena studied by the authors.

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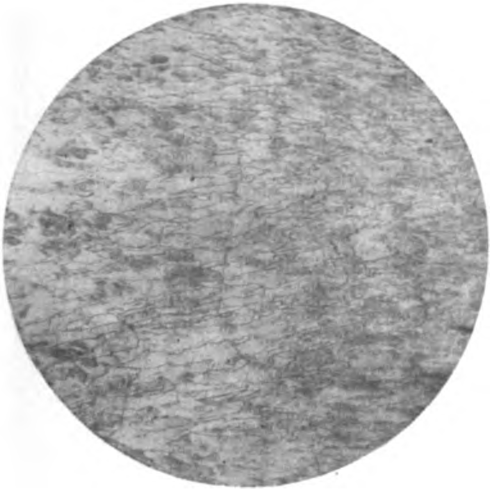

Fig. 1.—Cain's electrolytic iron as deposited. Section perpendicular to the electrode

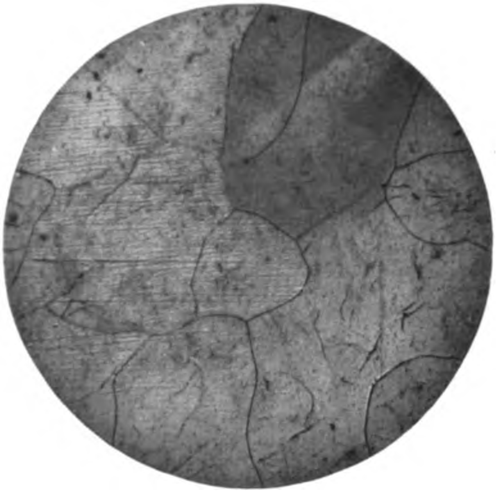

Fig. 2.—C. F. Burgess's electrolytic iron heated to 1050° C several times but not remelted

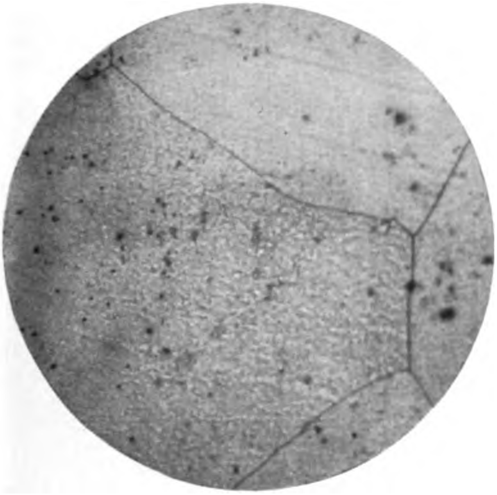

Fig. 3.—Same as Fig. 2, but at 500 x. Small bubbles are seen at this magnification

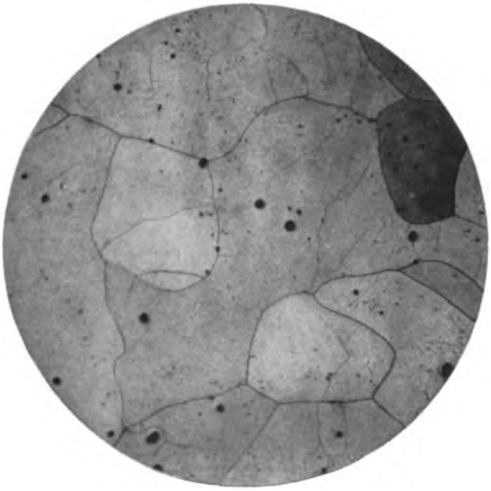

Fig. 4.—Cylinder F1, remelted from American ingot iron in gas furnace

Plate II.—*Photomicrographs*

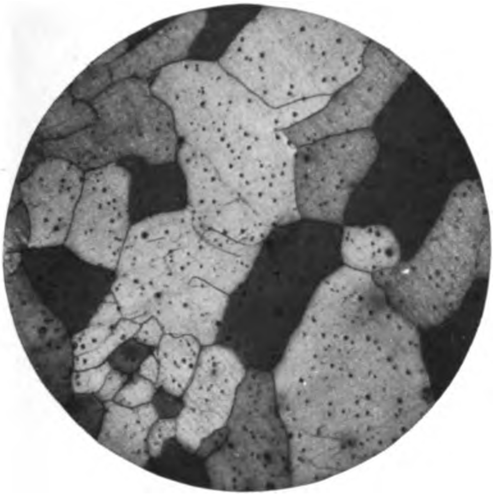

FIG. 5.—Cylinder F6. Cain's electrolytic iron, remelted in gas furnace

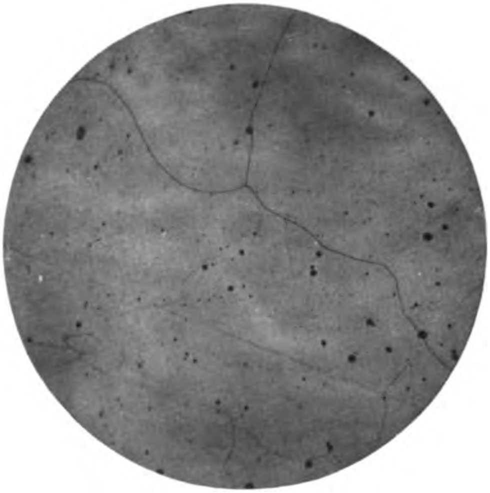

FIG. 6.—Cylinder 26 (Langheim-Pfanhauser) remelted in Arsem furnace in vacuo

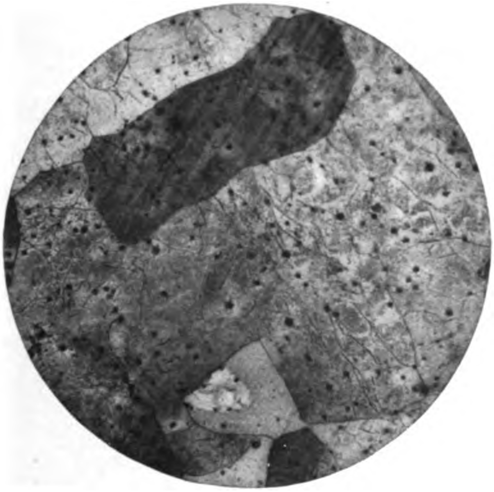

FIG. 7.—Cylinder F3 (Langheim-Pfanhauser) remelted in gas furnace

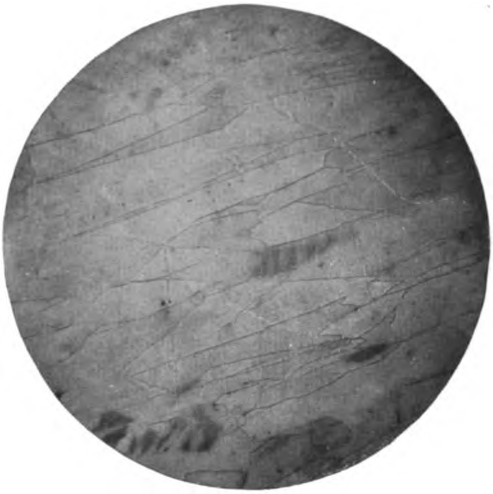

FIG. 8.—Same as Fig. 1, but 250 diameters

Plate IIa.—*Photomicrographs*

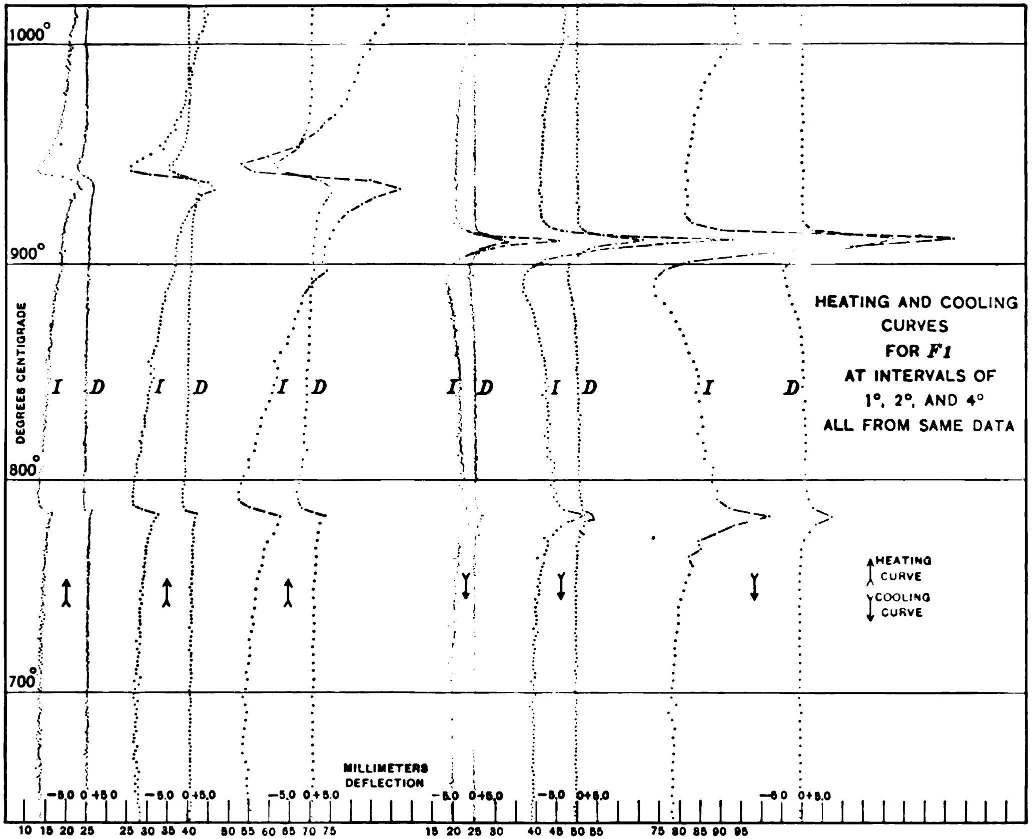

Plate III.—*Effect of different intervals*

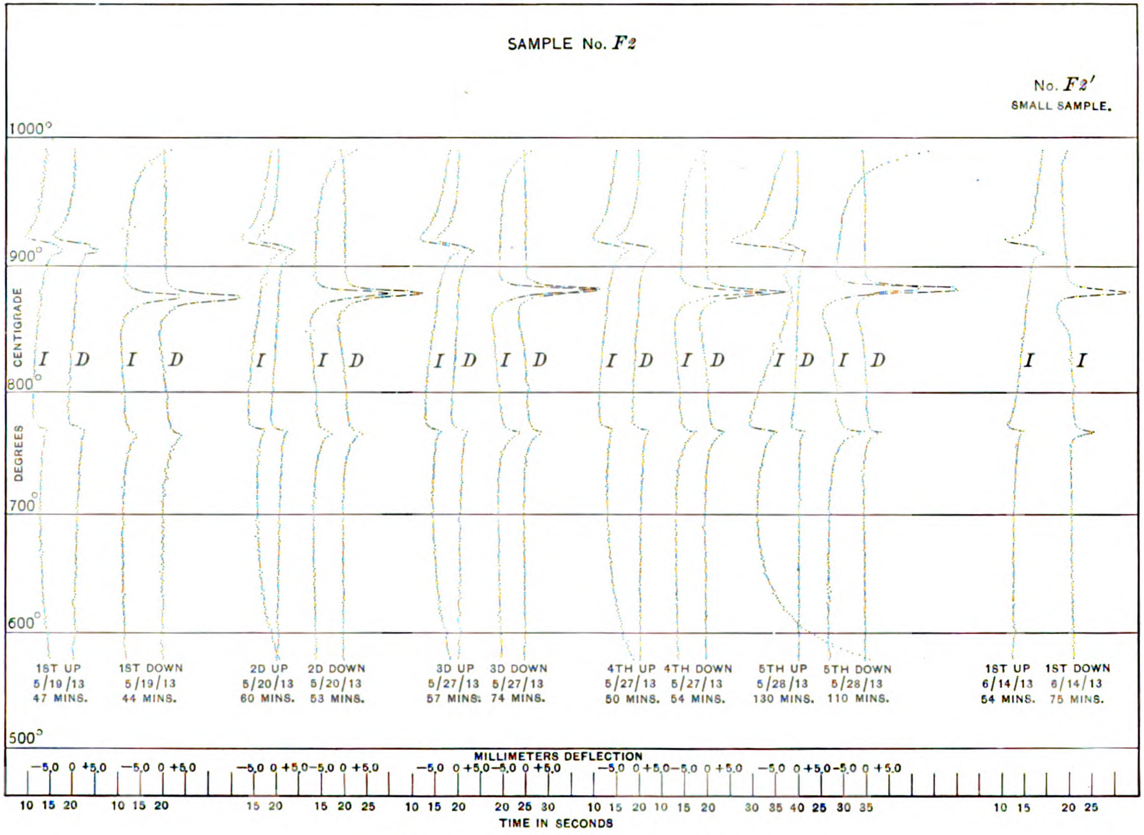

Plate IV.—*Curves for samples F2 and F2′*

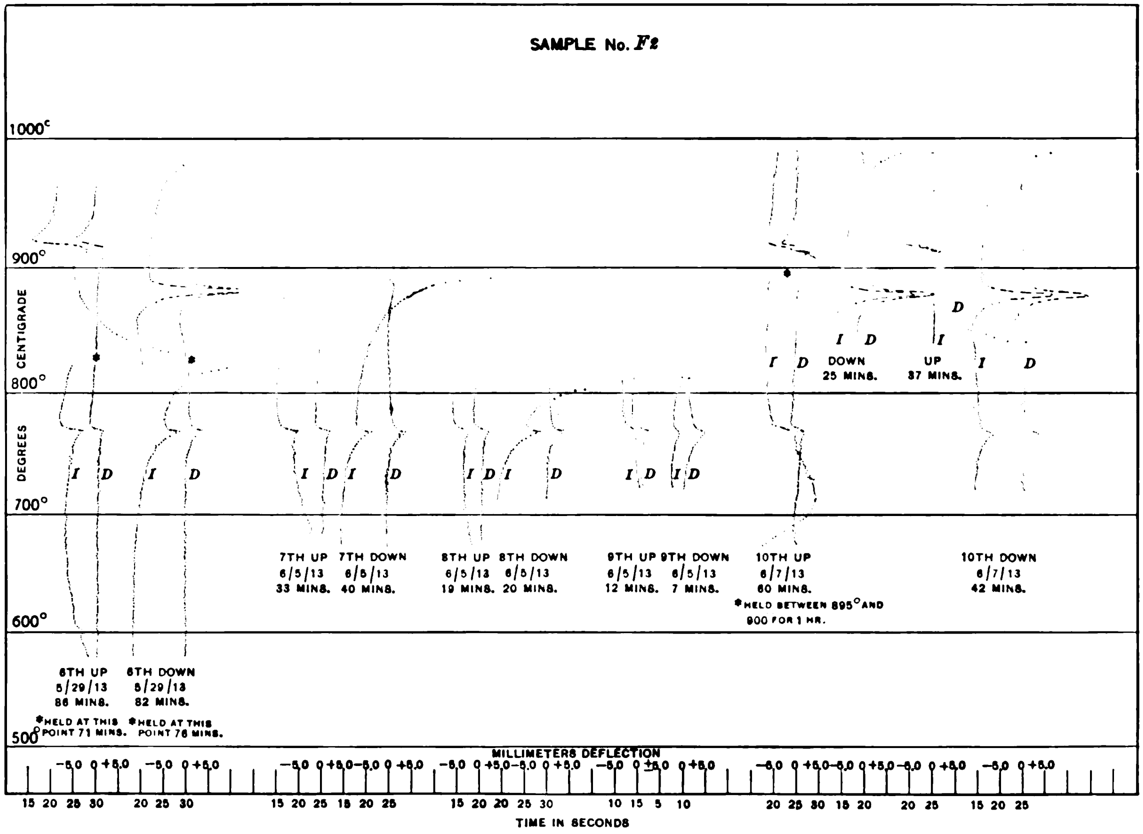

Plate IVa.—*Showing persistence of A2*

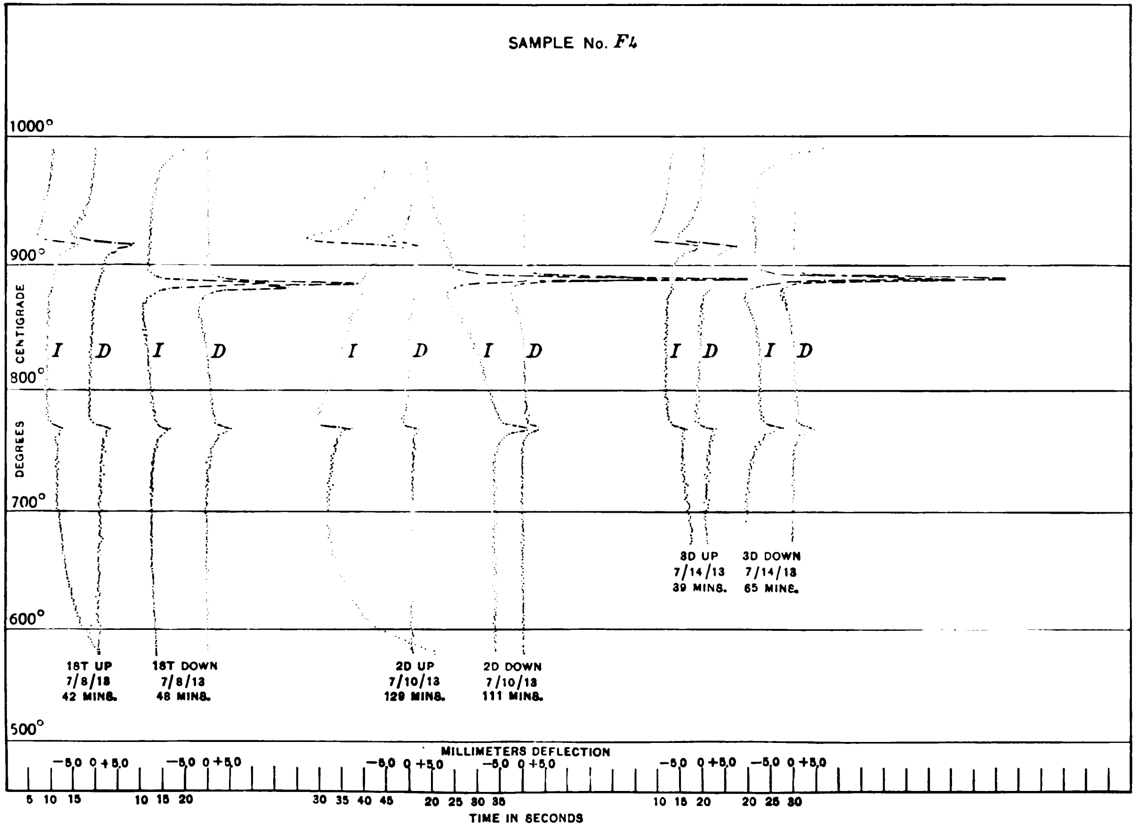

Plate V.—*Curves for sample F4*

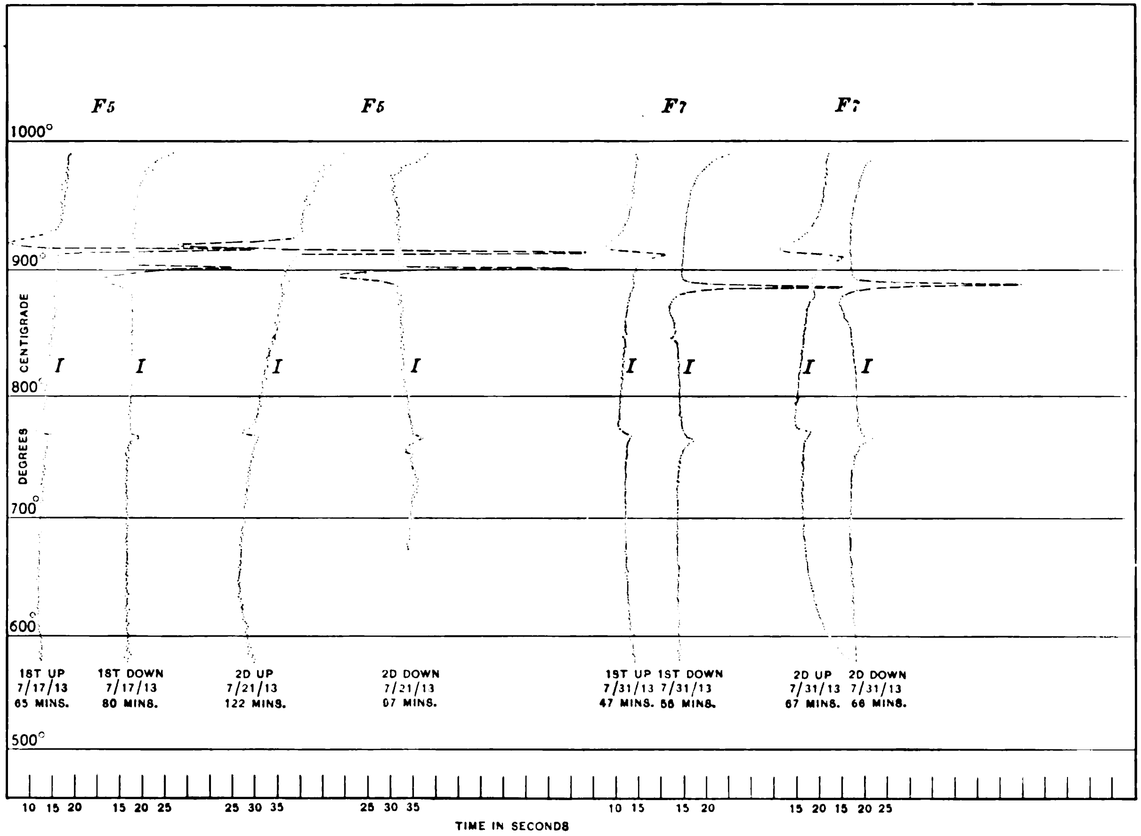

Plate VI.—*Curves for samples F5 (Carpenter's sample) and F7*

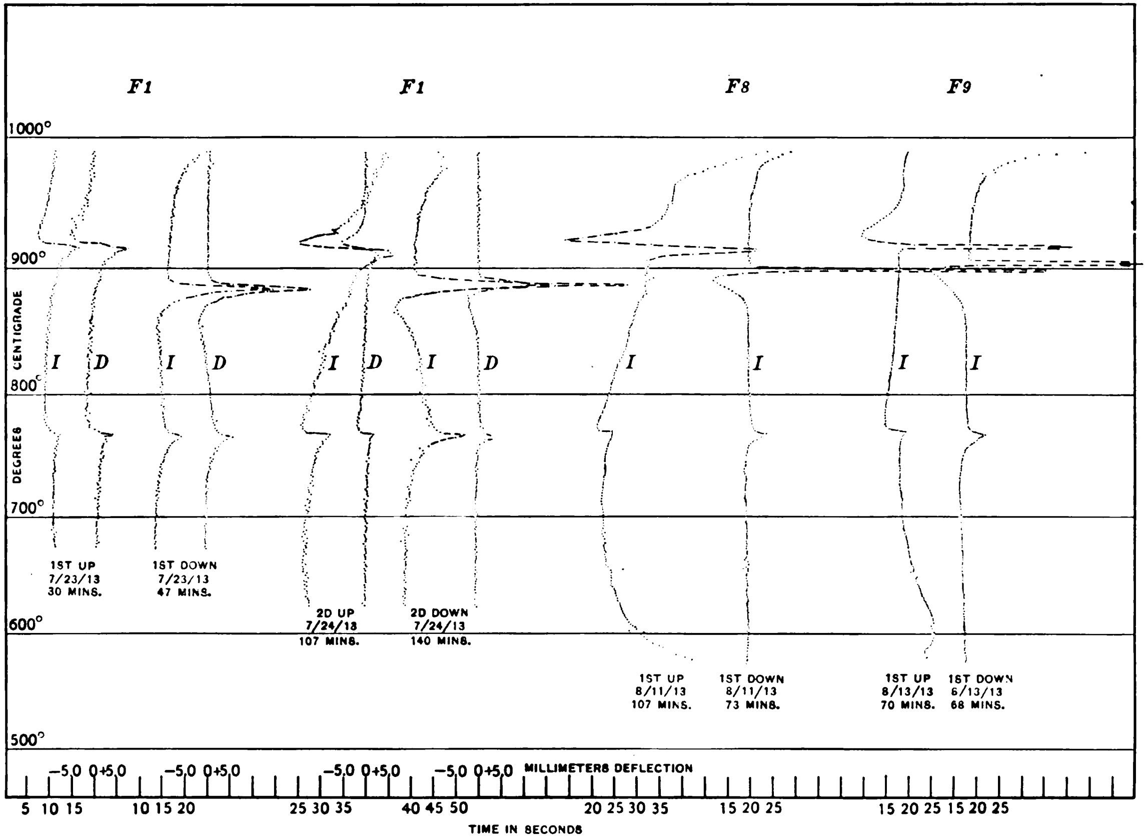

Plate VII.—*Curves for samples F1, F8, and F9*

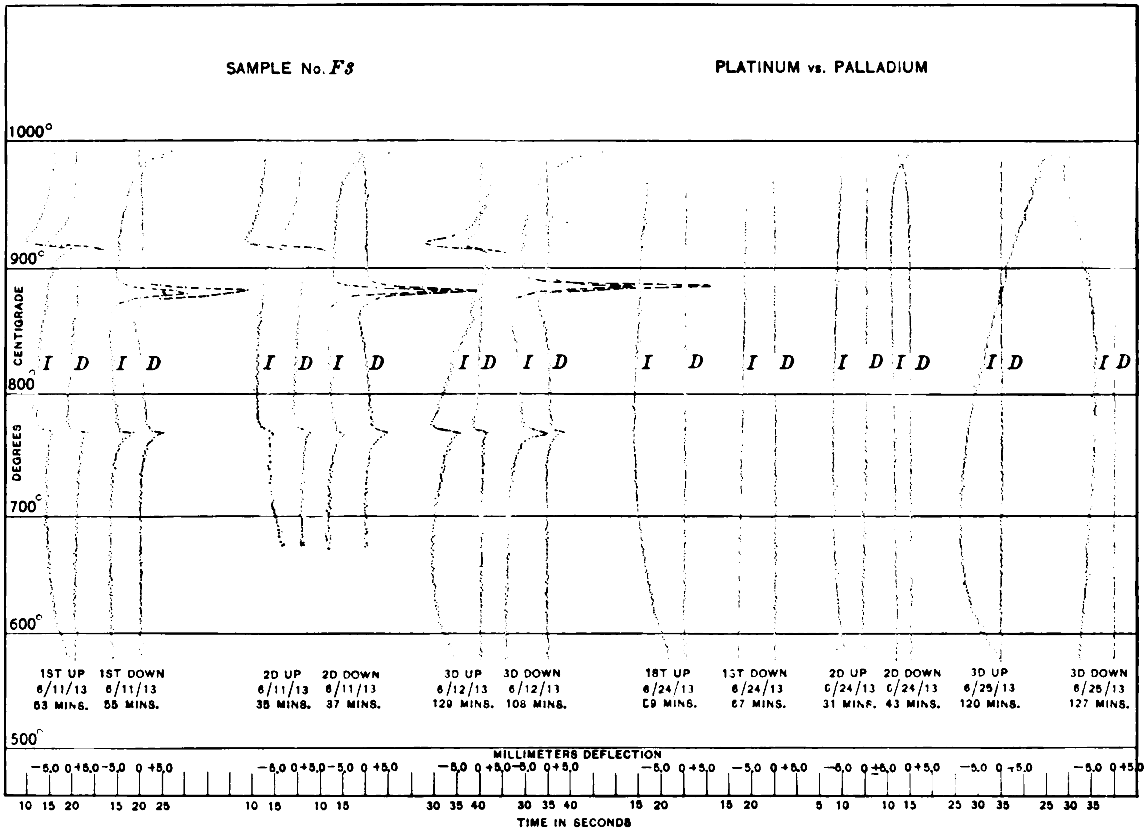

Plate VIII.—*Curves for sample F3 and Pt-Pd blank*

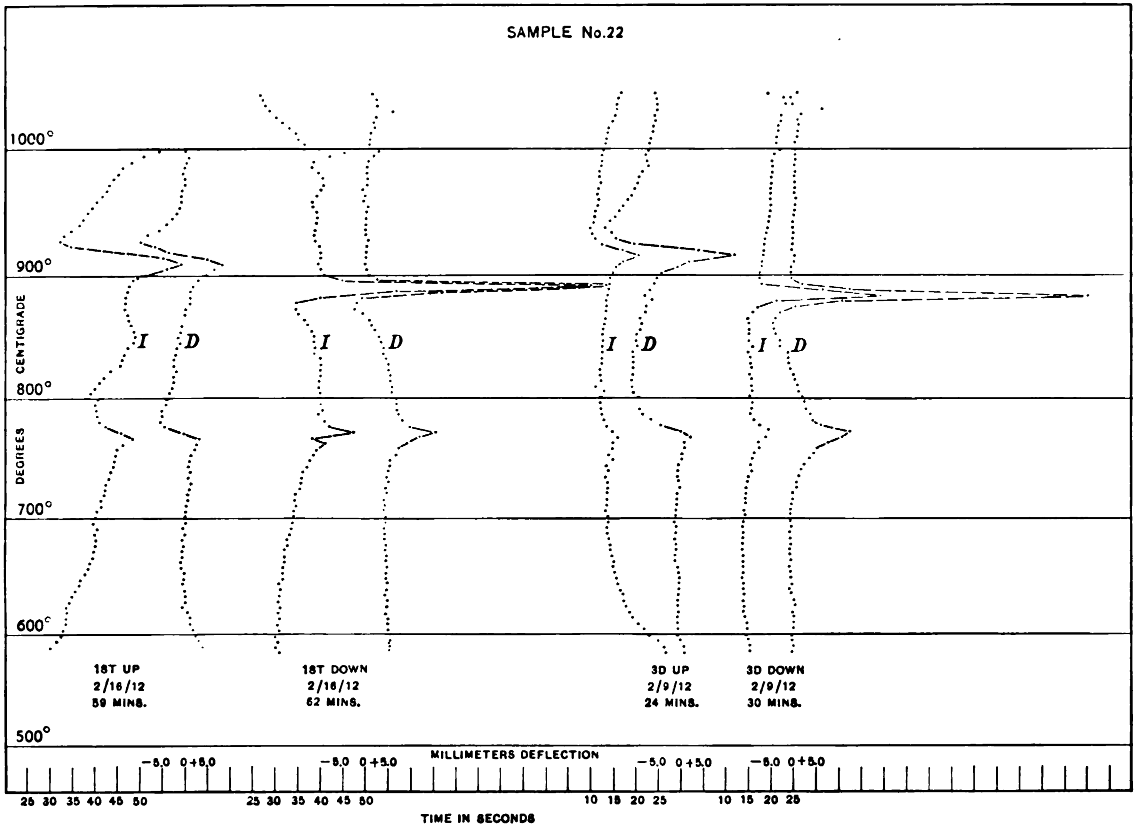

Plate IX.—*Curves for sample 22*

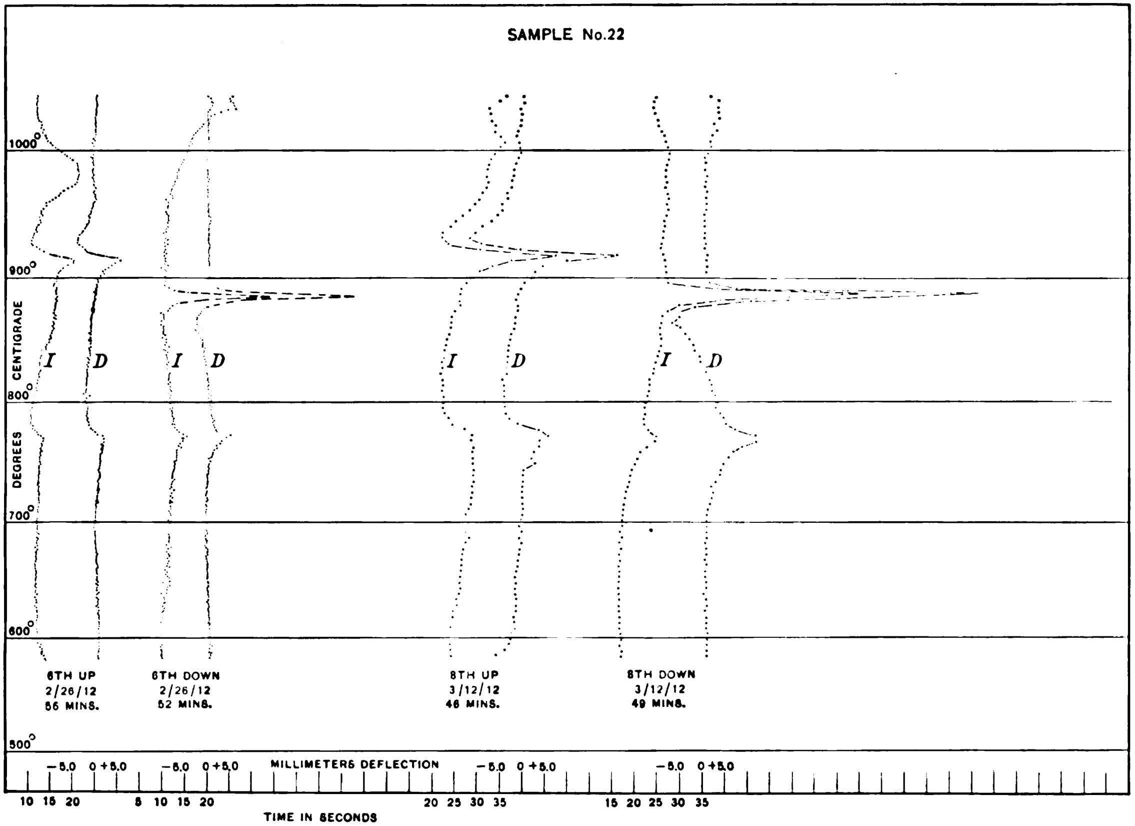

Plate IXa.—*Curves for sample 22*

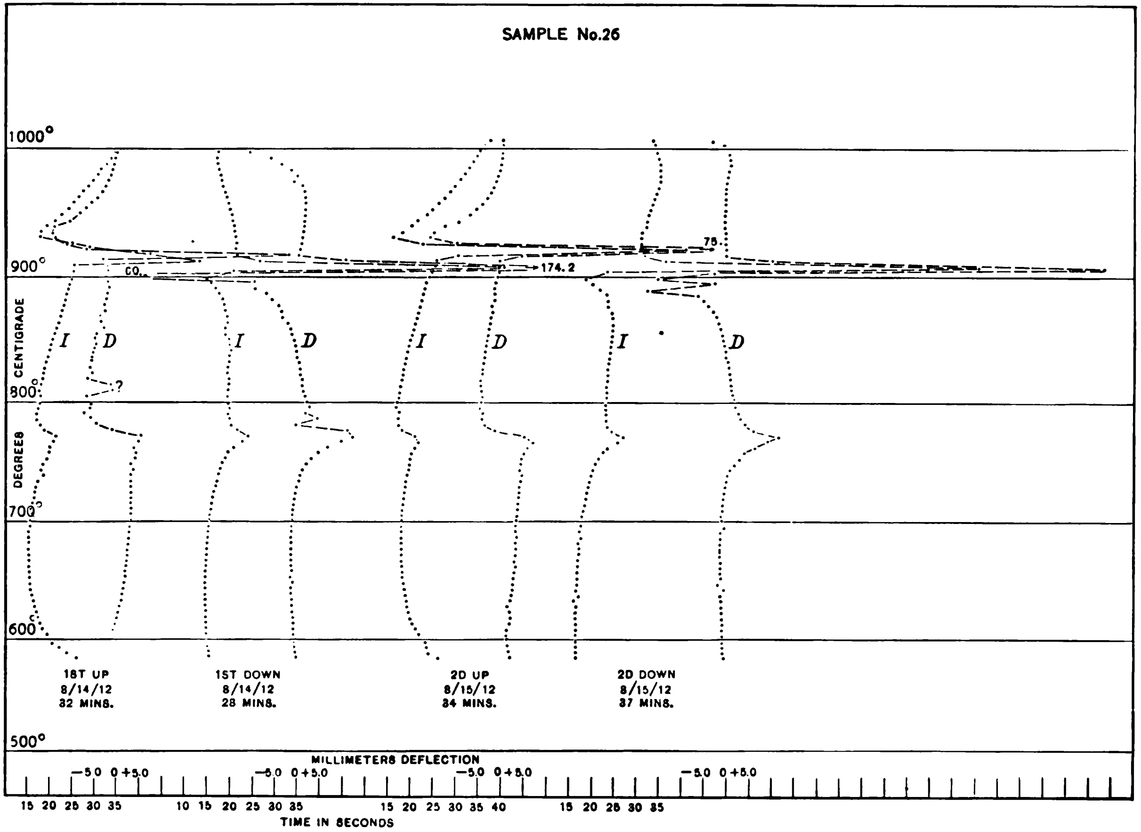

Plate X.—*Curves for sample 26*

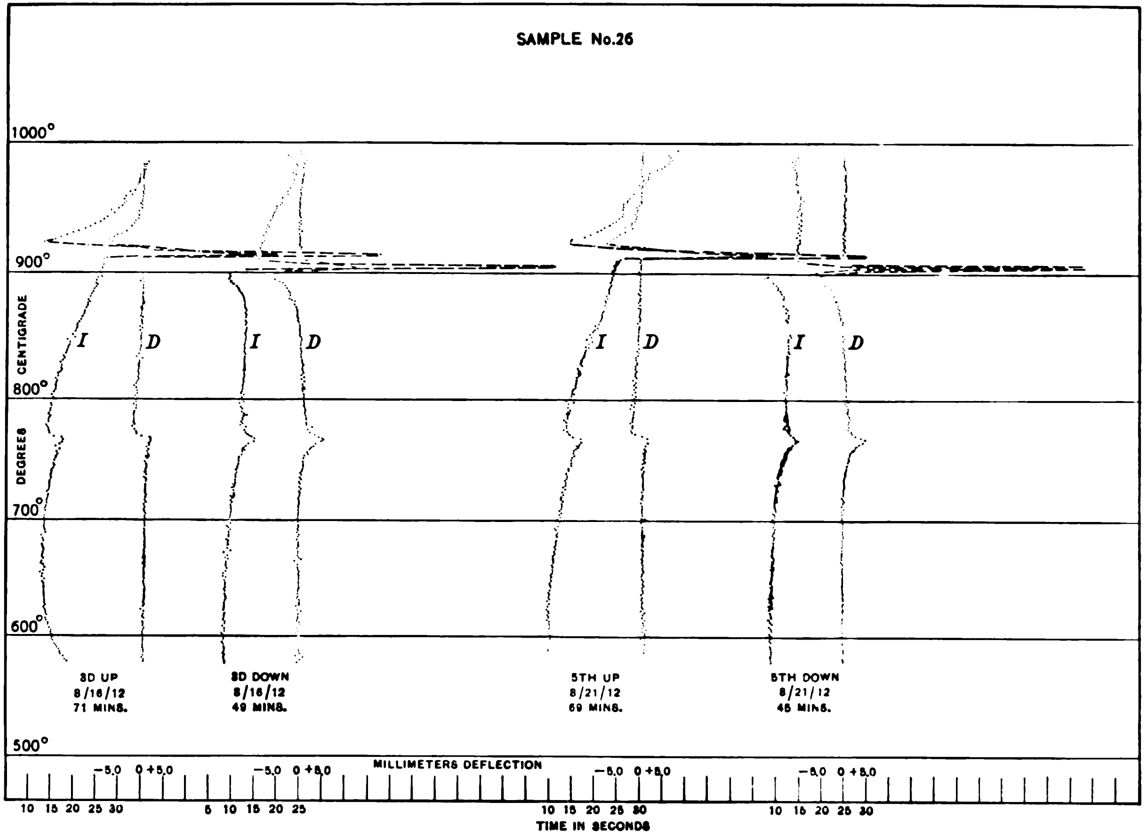

Plate X*a*.—*Curves for sample 26*

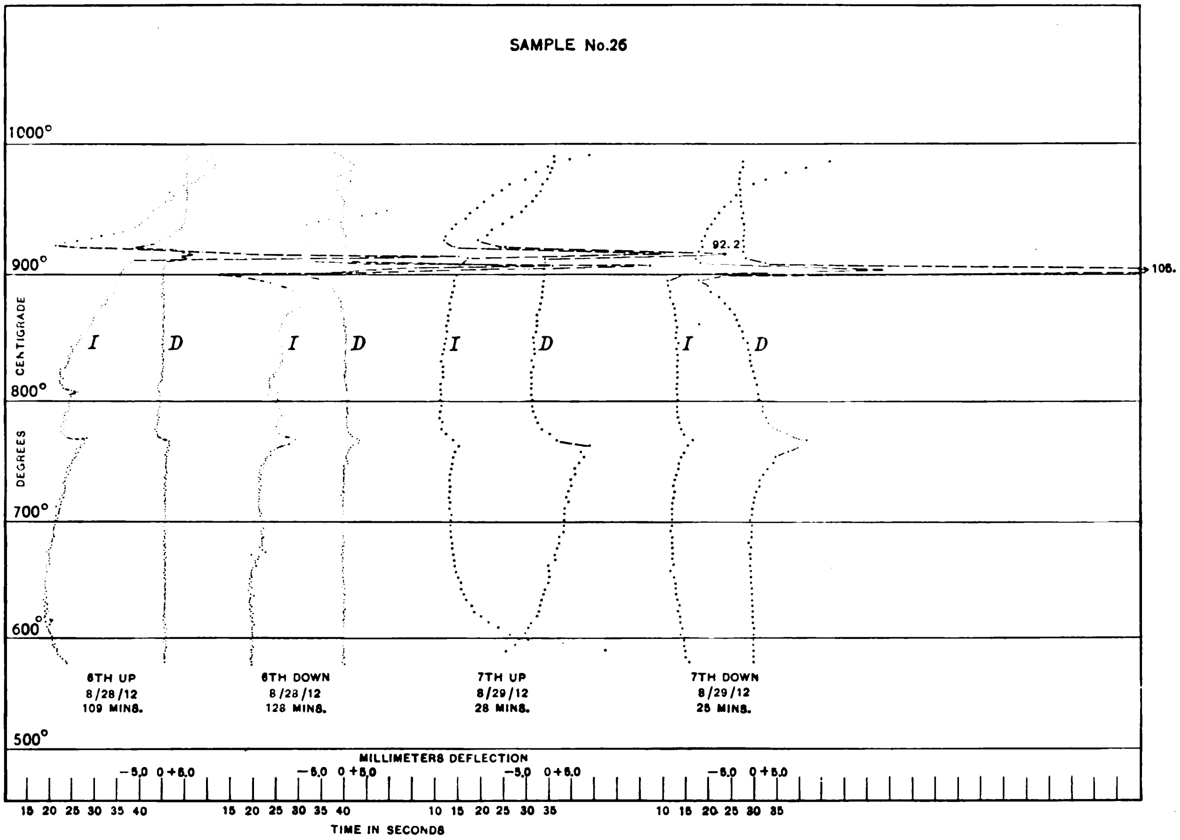

Plate X*b*.—*Curves for sample 26*

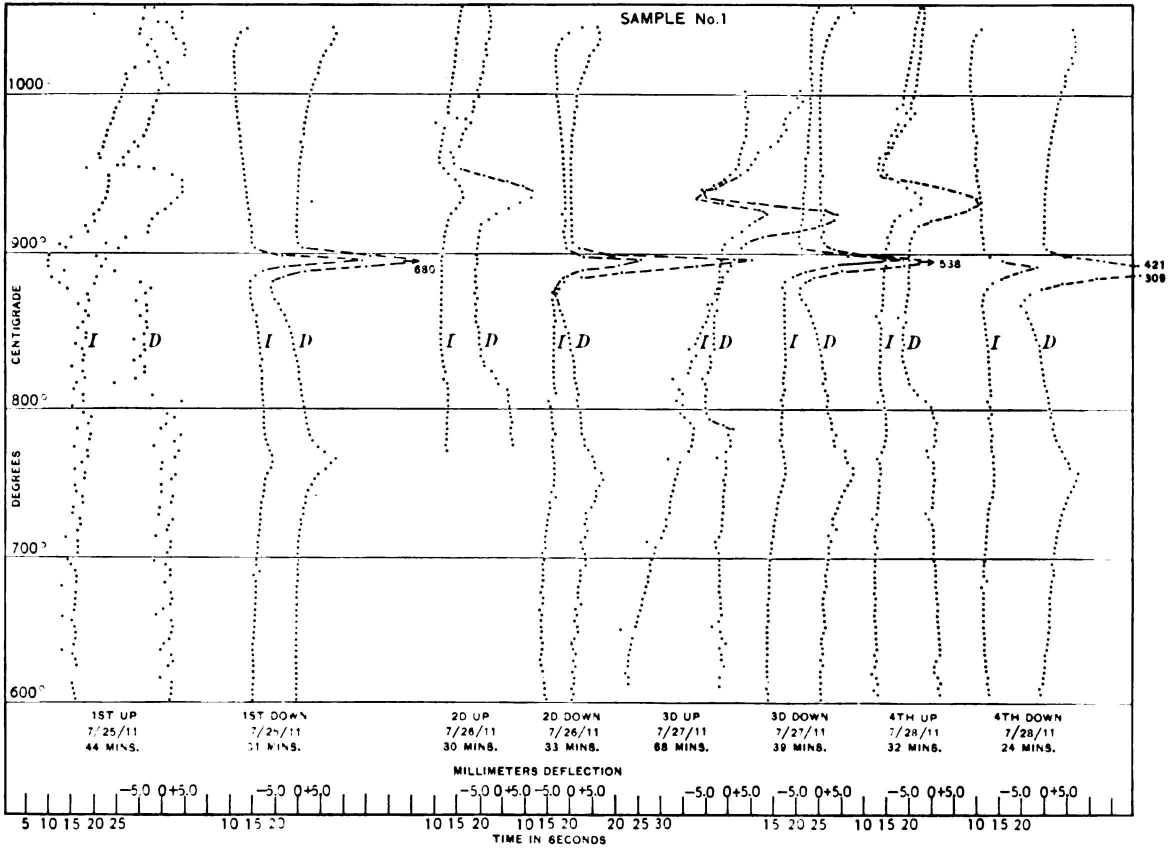

Plate XI.—*Curves for sample 1* (*first series taken*)

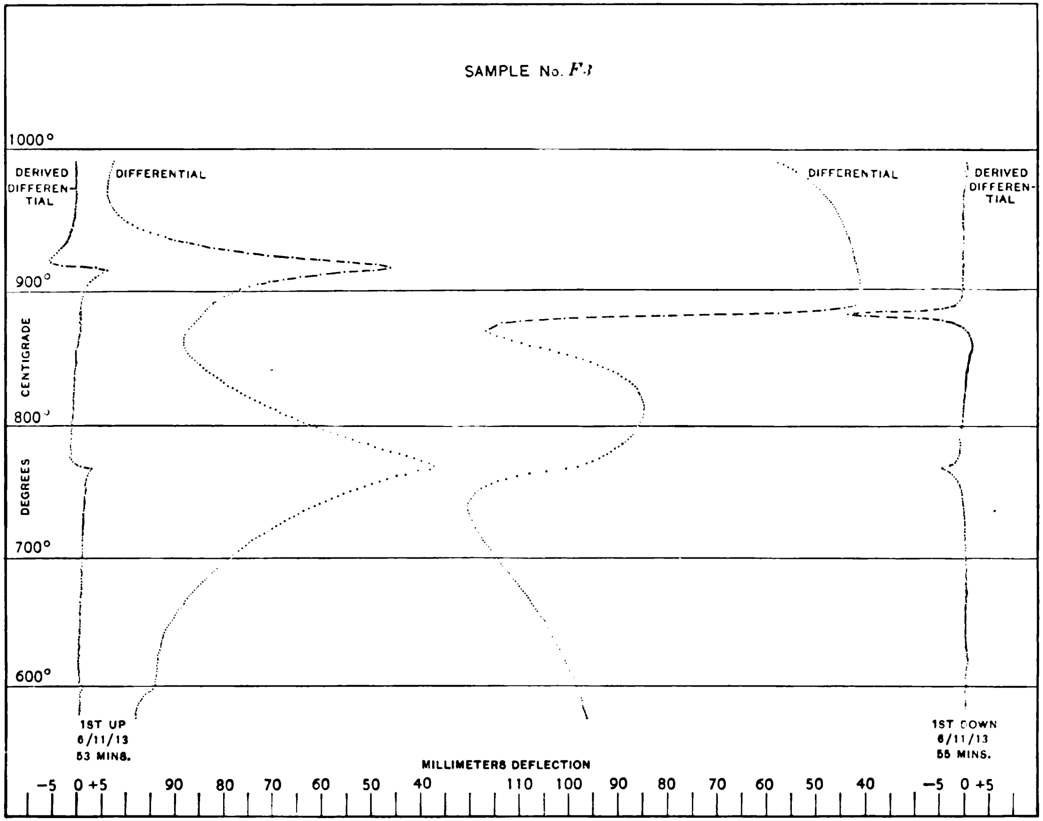

Plate XII.—*Comparison of differential and derived differential curves*

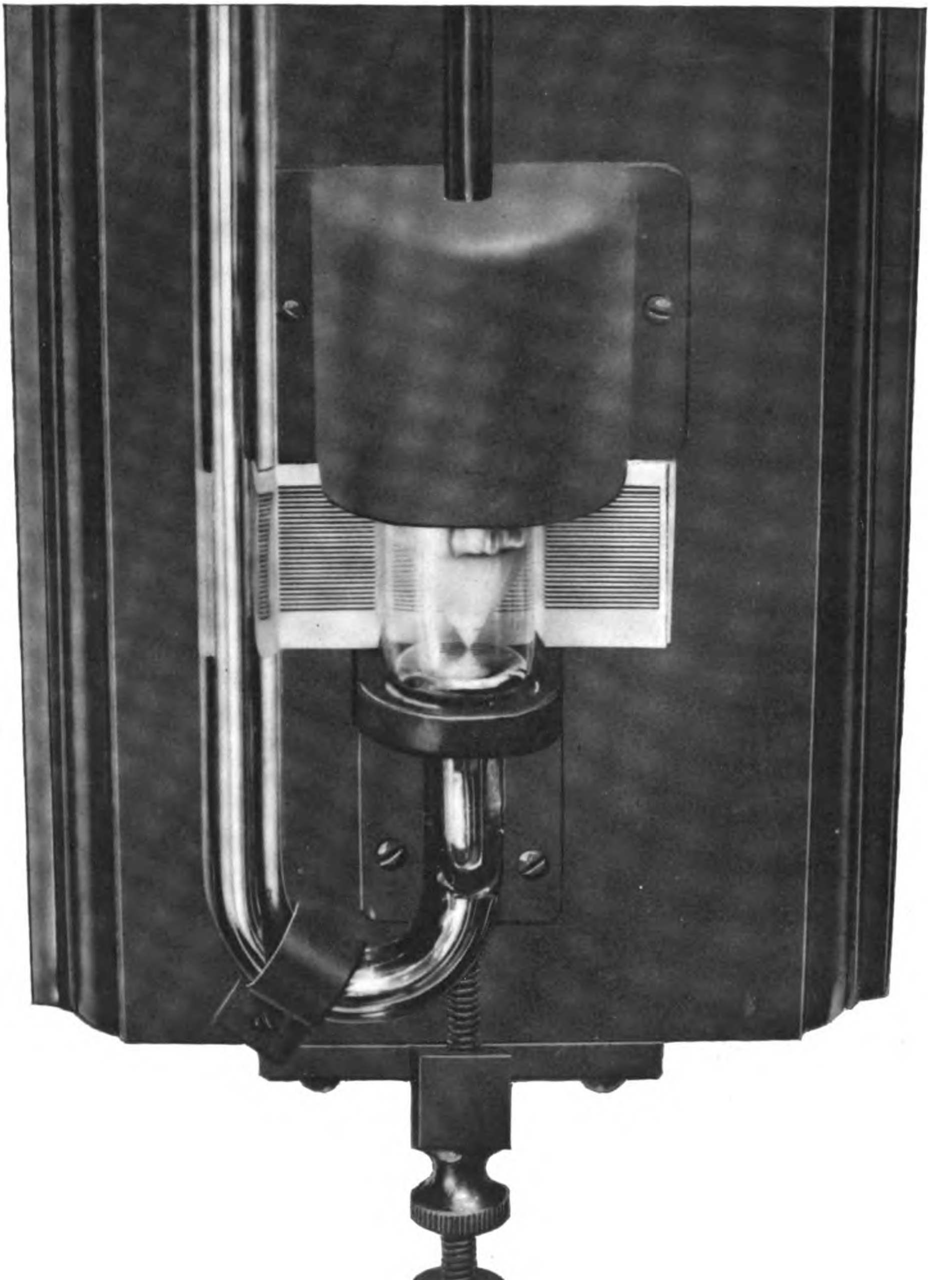

Fig. 1

NOTE ON THE SETTING OF A MERCURY SURFACE TO A REQUIRED HEIGHT

By M. H. Stillman.

The present brief article has to do with an improvement in the well-known method of adjusting a mercury surface to a given height by bringing it just into contact with the lower end of a pointer of ivory or other material which projects from above downward toward the surface of the mercury. This method is commonly made use of in certain types of mercurial barometers.

In setting the mercury surface in the cistern of a barometer it is usual to raise the surface of the mercury to the required height in order that the barometer may always be read with a rising meniscus, so as to reduce to a minimum the irregularity due to capillarity and to the sticking of the mercury to the sides of the tube. The mercury surface is therefore raised until the tip of the pointer and its image in the mercury seem to coincide or until a tiny dimple is formed in the mercury by the tip of the pointer.

The improvement referred to above is an artifice by means of which a smaller dimple can be detected, and consists simply of a scale of alternate parallel white and black lines, each about 0.5 mm wide, placed back of the pointer in such a way that the observer sees the image of this scale in the mercury surface at the point where the dimple is to be formed. When the pointer is not touching the mercury the surface of the latter will be practically plane, and the lines of the image of the scale will appear parallel; but, as soon as a very small dimple is formed by the contact of the pointer and mercury, the fact is made evident by a distortion of the lines of the image of the scale. The advantages apparent in the use of this auxiliary scale are the increased ease and accuracy with which the mercury surface may be set by using only ordinary care, and the consequent reduced eye strain when a large number of readings are made.

In Figs. 1 and 2 are represented the appearances of the mercury surface in the cistern of a barometer equipped with the above-mentioned auxiliary scale, before and after setting, respectively. It will be noted that while in Fig. 1, with the mercury below the end of the pointer, the lines of the image are practically parallel below the pointer, in Fig. 2 the images of the lines of the scale are distorted at the end of the pointer, indicating contact between the latter and the mercury. In Fig. 2, in order that the photograph might show the distortion of the lines more plainly, the mercury was set higher relative to the pointer than would be the case in an actual reading of the barometer.

In order to determine the accuracy with which settings of a pointer to the mercury surface may be repeated by this method, the experiment described below was made.

Fig. 3 is from a photograph of the apparatus used in the determination. A steel pointer (P) was attached to the foot of the movable scale (S) of a Zeiss vertical comparator and a slow-motion screw (A) adjusted to bear upon the upper end of this scale, so that the latter with the attached pointer could be slowly and steadily raised from or lowered to the mercury surface (M) below. B B are stretched rubber bands attached to the scale to maintain it in contact with the height-adjusting mechanism (A). The parallel-line scale (L) was placed behind the pointer, as shown, so that the desired reflection could be obtained in the mercury surface. The vertical scale (S) was read by means of the comparator microscope, which was provided with a micrometer eyepiece.

The steel pointer was a wire of about 1 mm diameter, with its lower end rounded to approximately a hemisphere of the diameter of the wire. Thus, the pointer was very similar in shape to those commonly used in mercury barometers, although, of course, not of the same material

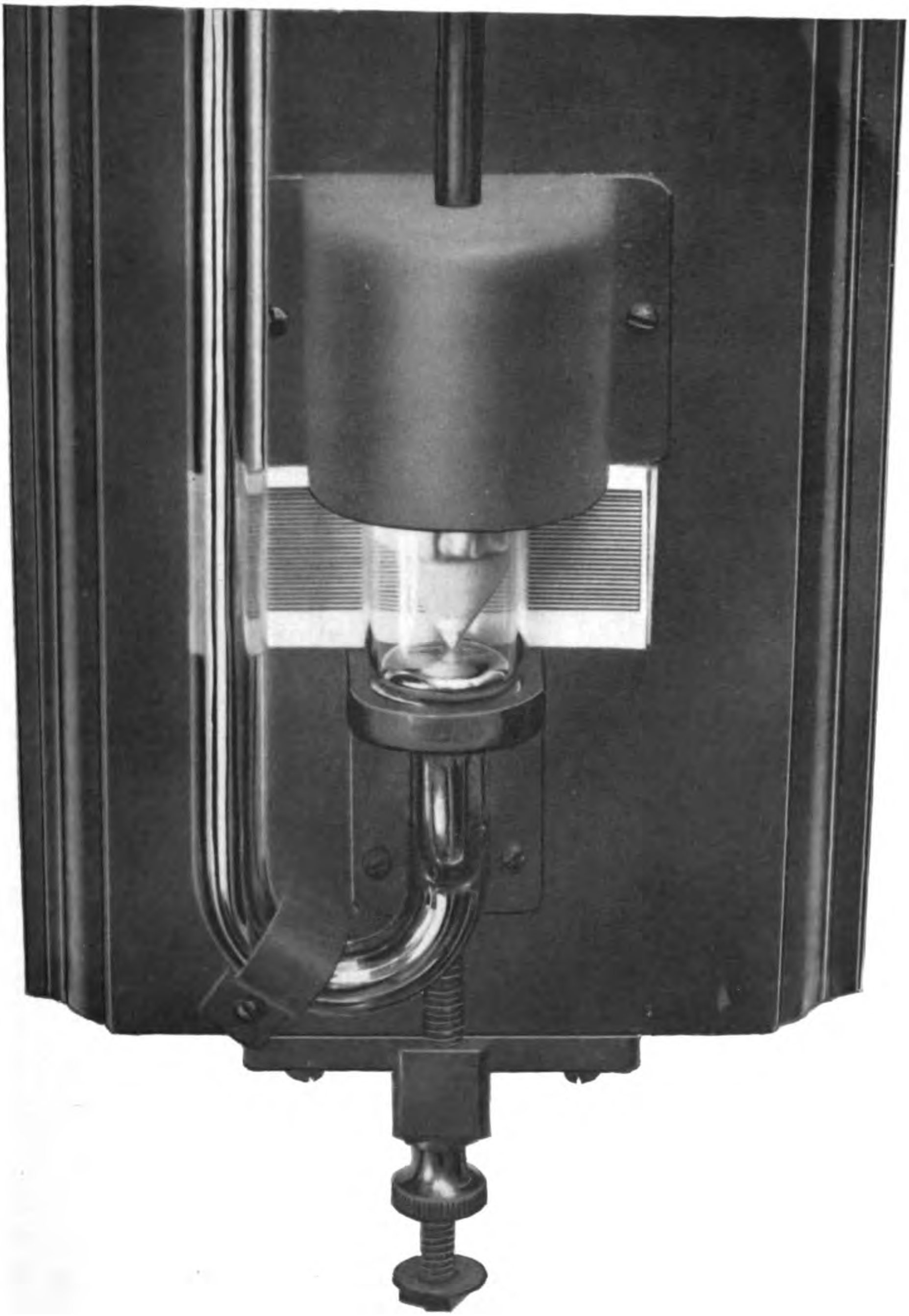

Fig. 2

The method of procedure in making the measurements was to lower the pointer slowly until a distortion of the parallel lines of the image was visible and then to read the scale by means of the micrometer microscope. No auxiliary device was used to aid the eye in detecting distortion of the lines.

Below is given a sample set of five consecutive readings made in the manner described above.

Number of observation	Reading at dimple contact	Deviation from mean
	mm	mm
1	46.8242	0.0003
2	.8242	.0003
3	.8239	.0000
4	.8232	.0007
5	.8242	.0003
Mean	46.8239	0.0003

This table indicates the rather surprising fact that all of the successive independent settings of the pointer and micrometer agreed with the mean setting well within 0.001 mm and that the average deviation from this mean was only 0.0003 mm. It was found that even better agreement of readings than the above recorded could be obtained when the illumination and the condition of the observer's eyes were more favorable.

The accuracy with which settings could ordinarily be reproduced, using the method of coincidence of point and image, was also investigated and found to be less than by using the improved method. Thus, while the average deviation of the settings from the mean in the case of the improved method was 0.0003 mm, the other method, under very favorable conditions, showed an average deviation of 0.0026 mm in a similar group of five settings.

It is of course to be expected that the height of the pointer (relative to the mercury surface), when set by the improved method, will be slightly less than when set by noting the apparent coincidence of the end of the pointer and its image or by noting when light can no longer be seen between the pointer and the mercury surface; in the settings by the two last-mentioned methods, the end of the pointer is probably slightly above the surface, while in the setting by the first-mentioned method (the improved method) the end of the pointer is necessarily a finite distance below the surface in order to produce the dimple. Determinations made with the apparatus described above indicated that this difference in the settings was ordinarily from 0.012 mm to 0.018 mm and that this improved method gives a setting between that of the ordinary dimple method and the method depending upon the apparent coincidence of the end of the pointer and its image. The above-mentioned differences are negligible in ordinary barometry but should be considered in extremely precise work if a barometer, the corrections of which are known to a high degree of accuracy, is used. The improved method should be especially valuable where it is practical to use it in determining the difference in height of two mercury surfaces; for in this case the constant errors of the settings cancel, thus allowing the full advantage of the sensitiveness of the method to be realized.

Unfortunately, not all barometers in which the lower mercury surface is set to the end of a pointer have been designed with sufficient space between the mercury surface and the top of the cistern to allow the improved method to be used with maximum advantage. There are, however, few barometers of this type with which considerable advantage both in convenience and precision of setting can not be gained either by placing the scale behind the cistern of the barometer or within it.

WASHINGTON, September 20, 1913.

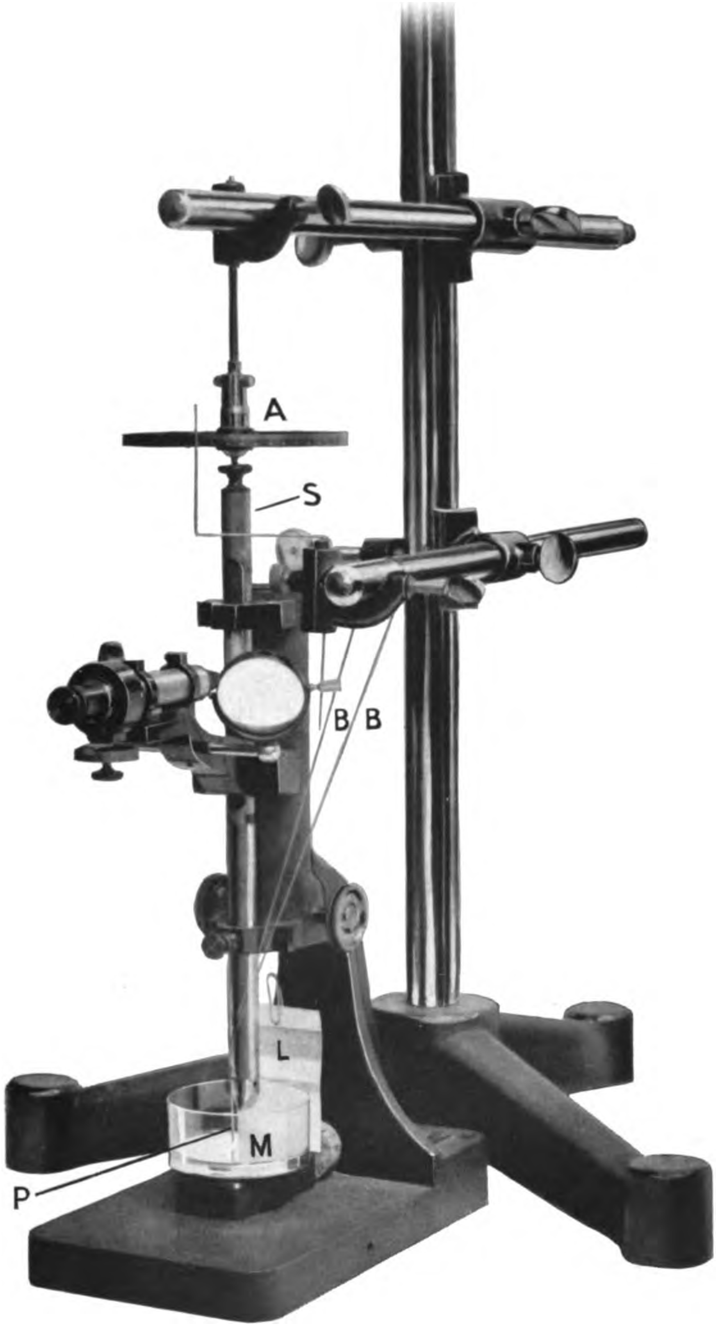

Fig. 3

MICROMETER MICROSCOPES

By Arthur W. Gray

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2. Methods of applying corrections to a group of micrometers 379
3. Determining the corrections of micrometer microscopes 384

1. SOME ERRORS AFFECTING MEASURING MICROSCOPES

Accurate measurements of length made with micrometer microscopes require careful consideration of the errors to which such instruments are subject.

The most important corrections to the readings of a screw micrometer are necessitated by the deviations from the nominal value of a division, the progressive errors, and the periodic errors. The last named may proceed from periodic irregularities in the thread (so-called drunken thread), failure to have the thrust bearings perpendicular to the axis of rotation, an eccentric drum, or an irregular division of the drum. With proper use no errors will be introduced by lost motion or by an irregularly distributed oil film. Temperature changes may cause variations in magnification by thermal expansion of the tube, the screw, or the microscope lenses (changing the curvatures), or by altering the refractivity of the media traversed by the light in forming the image measured by the screw. Then there are other irregularities too little understood to be subject to calculation. While these variations in magnification are measurable, they are, however, small and generally negligible. They are best taken into account by frequently measuring some known length interval.[1] In certain cases it may be necessary to correct for distortion of the image near the edge of the field. Again, serious errors may sometimes be caused by failure to focus accurately. Neither absence of parallax nor sharpness of image is a sufficient test.[2]

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[1] Mr. E. D. Tillyer of this bureau, to whom I am indebted for many valuable suggestions and criticisms, called my attention to a paper by F. L. O. Wadsworth, "On the construction of telescopes whose relative or absolute focal length shall be invariable at all temperatures," Roy. Astron. Soc. Monthly Notices, **62**, pp. 573–591; 1902. This discusses, with the aid of formulæ and illustrative examples, some of the sources of these variations of magnification, and it points out that when an ordinary flint and crown objective is mounted in a brass tube, the thermal expansion of the latter will almost compensate for the focal-length change of the former. Mr. Tillyer also tells me that it is a common practice in astronomical observatories to mount the objective so that its distance from the reticule can be varied sufficiently to permit adjustment of the magnification from time to time.

Another possible trouble deserves to be mentioned, because if existent it may prove very exasperating and may long evade detection. Any holes in the surfaces of the thrust bearings, even if extremely small, may harbor minute chips or grains of dust, which in time work between the rubbing surfaces and cause large irregularities of a more or less periodic nature. When such trouble appears in a comparator, its periodic nature is apt to remain unnoticed, and the irregularities are likely to be ascribed to such things as a loose joint somewhere in the framework supporting the microscopes, a bad place in a micrometer screw, or something rubbing against one of the spider lines.[3]

The elusive nature of such troubles is well illustrated by an experience recorded by Hough,[4] who succeeded Sir David Gill in charge of the Cape Observatory. After reporting the satisfactory behavior of some underground reference marks for the new meridian circle, Hough states "The discussion of azimuth determinations made during the year 1906 and the early part of 1907 indicated, however, that though the marks themselves seemed to possess all necessary stability, the azimuth determinations were affected by a persistent and apparently increasing systematic difference amounting at the time to $0^{s}.1$ in azimuth, depending on whether the observations were made with instrument in position Clamp East or in position Clamp West. The difference was eventually traced to a loose jewel in the end bearing of the micrometer screw, since the resetting of which the discordances seem to have entirely disappeared."

---

[2] Curious anomalies, finally traced to inaccurate focusing, long puzzled Fizeau and Tresca of the French Section and Bosscha and Oudemans of the Dutch Commission while comparing line standards with the Mètre des Archives, an end standard. An explanation was given by Fizeau, and a method of reducing the trouble pointed out by Cornu and used in comparing the Mètre des Archives with the provisional international standard. (See A. Cornu and J. R. Benoît, "Détermination de l'étalon provisoire international." Trav. et Mém., **10**, p. 9, 1894; W. Foerster, "Ueber den Anschluss des älteren Urmaasses und der Copieen desselben an das neue Deutsche Prototyp für das Meter," Norm. Aich. Komm. Abhandl. **1**, p. 67, 1895; J. R. Benoît: "Mesures de dilatation et comparaisons des règles mètriques," Trav. et Mém., **2**, C. 26, 1883; A. Hirsch, "De l'influence de la mise au foyer sur la valeur du micromètre d'un microscope," Proc. verb., p. 255, 1877; and W. Foerster, "Note sur l'influence de la mise au foyer et de l'inclinaison des microscopes sur les mesures micrométriques," Proc. verb., p. 271, 1877.) That Cornu's procedure, however, merely reduced but did not eliminate the trouble unless aplanatic objectives (free from spherical aberration and coma) were used seems to have been recognized first by Benoît and Guillaume after obtaining systematic differences of nearly 4 μ in comparing length standards by two different methods. (See J. R. Benoît and C. E. Guillaume: "Mètres à bouts," Trav. et Mém., **12**, p. 35, 1902.) These experiences seem to have pretty generally escaped the notice of those who write treatises as well as of those who use micrometer microscopes. Errors of 10 μ or more may be easily introduced by inaccurate focusing even though repeated pointings may differ by less than 1 μ.

[3] In a case which caused the writer considerable annoyance the thrust bearings were found deeply scored and a grain of dirt embedded near the edge of a minute cavity due to porosity of the metal. Apparently in wiping the surfaces during the cleaning that preceded calibration, particles of dirt had been brushed into some of the cavities only to work out into the bearings when the micrometer was used. Removing the embedded dirt speck still left the periodic error about five times as great as when the microscope was calibrated. A careful grinding of the bearings reduced the error to about the value at the time of calibration. Attempts at further improvement by polishing only made matters worse. Of course an entirely new calibration was necessary after a thorough cleaning, with special attention to cavities. After this experience each micrometer drum and bearing was covered by a dust-excluding case with a celluloid window. This cover also prevents the silver of the drums from tarnishing and has the further advantage of eliminating blunders when reading the tenths of a turn, since the windows are only twelve divisions long and, therefore, show but one figure at a time except when the setting is close to an exact tenth.

[4] Report of His Majesty's Astronomer at Cape of Good Hope for the years 1906 and 1907, pp. 3-4.

TABLE 1

	A	B	C	D	E
1	+151	−38	−1	−8	−15
2	+102	+27	0	+1	− 9
3	+101	−21	+1	+8	+12
4	− 40	−49	+1	+7	+ 9

Table 1 is given to show the magnitudes of the periodic errors found in some microscopes. On the assumption that the micronometers read correctly at the beginning and at the end of a turn, the corrections in ten-thousandths of a turn that must be added to the reading at the end of each fifth indicated in the first column are recorded in the other columns. Under A are the corrections for one turn of the microscope referred to in the footnote on page 376, after it had been repaired as well as possible. Under B are those found for a turn of a microscope used in making important length measurements. The instrument had never before been investigated. A curious feature of this microscope was the regular repetition of this series of corrections every other turn, with a somewhat different but equally regular series for the alternate turns. Column C represents a screw of unusual excellence, made by an American firm noted for high-grade astronomical instruments. D represents the average and E the worst of a group of 10 others made by this same firm. The irregularities which these 10 exhibit are of the same order of magnitude as those of the best microscopes belonging to the International Bureau of Weights and Measures.

As a final word of caution it should be noted that whenever high accuracy is demanded in measurements made by micrometer microscopes the screw errors should be investigated periodically. It is by no means safe to assume that screws in use will remain unchanged indefinitely. Not only can irregularities creep in without detection, but even the regular wear of the threads (especially when the screws are new) can produce marked changes in the errors. This seems to have been pointed out first by Christie.[5] Subsequently Gill investigated the effect of wear on gun-metal micrometer screws working in brass bearings.[6] Errors originally negligible had in the course of a little more than four years increased to such an extent that when different parts of the screws were used to measure the same length, covering about 4.8 turns, discordances as great as from 0.02 to 0.09 of a turn were obtained with the same micrometer, averaging as much as 0.04 turn for the six screws examined. In a later paper[7] he shows that "even when steel screws are employed the changes produced by wear in the non-periodic corrections are very marked," although "the wear of steel screws in brass bearings is very much less than that of gun-metal screws in brass bearings."

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[5] W. H. M. Christie: "On the effect of wear in the micrometer screws of the Greenwich transit circle," Roy. Astron. Soc. Monthly Notices, **37**, pp. 18–22; 1876.

[6] David Gill: "On systematic errors in the readings of the circle microscopes of the Cape transit circle," Roy. Astron. Soc. Monthly Notices, **45**, pp. 64–90; 1884. In this paper and also in a later one (Monthly Notices, **45**, pp. 432–444, 1885) Gill gives numerous reasons to show that what he considered serious errors in the Cape Catalogue of 1880 (embracing observations between 1870 and 1879), which had been attributed by the author, Mr. Stone, to constraint caused by imperfectly finished threads at the ends of the screws, were in reality caused by the wear to which the screws had been subjected since they were brought into use in 1855.

[7] David Gill: "Note on the effect of wear on the errors of micrometer screws," Roy. Astron. Soc. Monthly Notices, **59**, pp. 73–76; 1898.

2. METHODS OF APPLYING CORRECTIONS TO A GROUP OF MICROMETERS

Fig. 1 is presented for the purpose of recalling the relation between the length l to be measured and the observations made with the microscopes. The vertical arrows represent the optical axes of the two microscopes of a transverse comparator. The inclined arrows represent the axes of the pencils forming images of the lines defining the extremities of l. y is the distance between the points O_L and O_R on which the microscopes would be sighted when the micrometers read zero (if they could be moved that far). L and R are the distances from O_L and O_R, respectively, to the ends of l, and are given directly by the micrometer readings corrected to measure lengths in terms of the same unit. Then

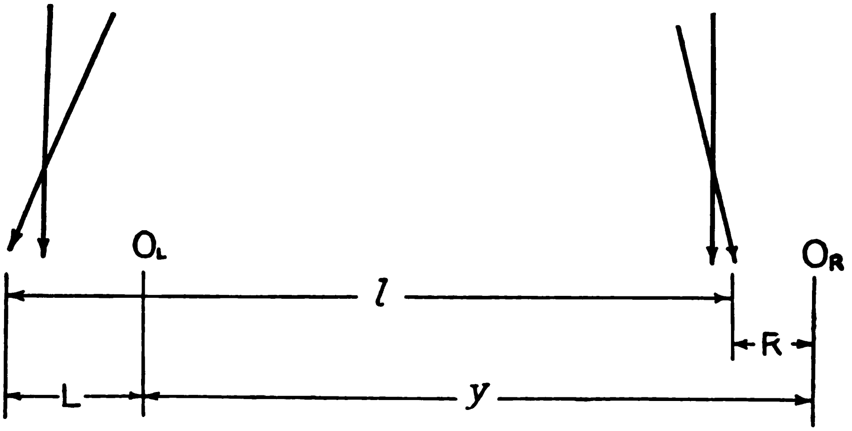

Fig. 1.—*Principle of microscope comparator*

$$l = y + (L - R) \qquad (1)$$

The distance y must be determined or eliminated by comparing l with a known length. Let the subscripts A and B indicate measurements made on two bars to be compared. Then it follows that

$$l_A - l_B = (L_A - R_A) - (L_B - R_B) \equiv (L_A - L_B) - (R_A - R_B) \qquad (2)$$

If the uncorrected readings of the micrometers are indicated by primes and the corrections by Δ's, then

$$
\begin{array}{ll}
L_A \equiv L'_A + \Delta L_A & R_A \equiv R'_A + \Delta R_A \\
L_B \equiv L'_B + \Delta L_B & R_B \equiv R'_B + \Delta R_B
\end{array} \qquad (3)
$$

If the progressive and the periodic errors are so small that it is sufficient to apply only the scale-value factor, the second of equations (2) is the more convenient. But in work demanding the highest accuracy it is by no means justifiable to omit the corrections for progressive and periodic errors unless investigation shows that the screws are of unusual excellence. However, the labor involved in applying, as well as in determining, these corrections by any of the methods ordinarily described is sufficient to discourage their use in all but very exceptional cases.

The writer has developed a method which takes into account all necessary corrections, but with an expenditure of labor after the microscopes have been calibrated once for all even less than that required to multiply the change in each micrometer reading by the mean scale-value and subtract. Essentially it is a simplification of the procedure followed by the International Bureau of Weights and Measures in measuring the national prototype meters.[8] The principal gain is effected by reducing to two tables (both of which can be mounted on a single card) all the information contained in the six tables used by the International Bureau. A simplified method of computing the tables will be discussed in the next section. The table for the left microscope gives at one inspection the total correction ΔL that must be added to any reading L' of the left microscope to give the corrected reading L that appears in equations (1), (2), and (3), above; that for the right microscope gives $-\Delta R$, the negative of the total correction to the reading R'. Reversing the sign of ΔR is merely a matter of convenience. It is usually sufficient to enter the corrections for every tenth of a turn and to obtain those for the hundredths by interpolation. A convenient arrangement is one similar to that followed in most mathematical tables—the whole turns are indicated at the side and the tenths at the top.

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[8] J. R. Benoît: "Mesures de dilatation et comparaisons des règles métriques," Trav. et Mém., 2, C. 131; 1883. The original observations are recorded on p. C. xix. and the tables for correcting the microscope readings are to be found on pp. C. xi.-xiv.

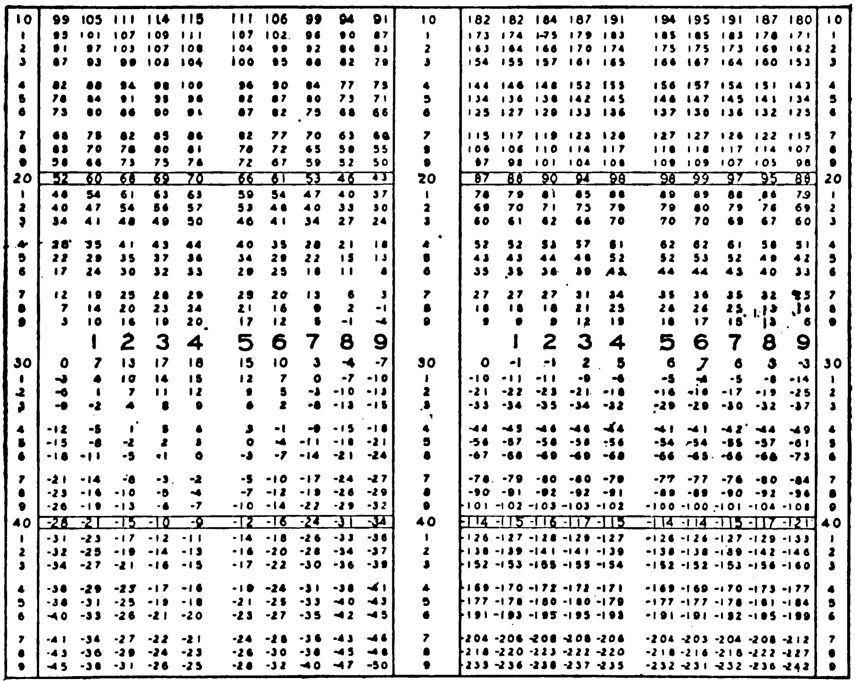
The displacement corresponding to one division (=0.01 turn) of the microscopes may differ so little from 1 μ that only small corrections will be required to reduce the readings to microns. It may, however, well happen that reduction to the desired length unit might require corrections so large as to be inconvenient. It then becomes advisable to select an auxiliary unit corresponding to the average screw value, and to express all corrections in terms of this unit, which should be the same for both microscopes.[9] It is further advantageous to minimize the magnitude of the corrections by adjusting both microscopes to give almost the same magnification—if possible one that permits a simple reduction factor. Then all computations can be made in terms of the auxiliary unit, multiplying by the reduction factor being deferred until the end.

By way of illustration Table 2 is presented, which contains all the corrections to the two microscopes discussed in the footnote on page 376. The arrangement is that indicated in the second paragraph before this. The auxiliary unit selected was 3/4 μ, since one drum division had nearly this value. Since the construction of the microscopes (with fixed tubes) made adjustment of the magnification inconvenient, it was omitted. The unit in which the corrections are expressed is 1/10 division = 3/40 μ. For convenience, each microscope was assumed to have no error at the beginning of turn number 30, which was the center of the range. Since these microscopes were used for measuring large elongations, the calibration was extended over 40 turns, embracing about four-fifths of the field of view. If each microscope had been adjusted to give the most convenient magnification, no number greater than 30 would have appeared in the table; and the corrections for readings near the middles of the screws would have been considerably smaller than this.

---

[9] All these considerations apply with increased force to a larger group of microscopes, for example, a group of four used to read a divided circle, or several used to step off a considerable length by means of a bar reaching from one microscope to the next.

TABLE 2



10	99	105	111	114	115	111	106	99	94	91	10	182	182	184	187	191	194	195	191	187	180	10
1	95	101	107	109	111	107	102	96	90	87	1	173	174	175	179	183	185	185	183	178	171	1
2	91	97	103	107	108	104	99	92	86	83	2	163	164	166	170	174	175	175	173	169	162	2
3	87	93	99	103	104	100	95	88	82	79	3	154	155	157	161	165	166	167	164	160	153	3
4	82	88	94	98	100	96	90	84	77	75	4	144	146	148	152	155	156	157	154	151	143	4
5	78	84	91	95	96	92	87	80	73	71	5	134	136	138	142	145	146	147	145	141	134	5
6	73	80	86	90	91	87	82	75	68	66	6	125	127	129	133	136	137	138	136	132	125	6
7	68	75	82	85	86	82	77	70	63	60	7	115	117	119	123	128	127	127	126	122	115	7
8	63	70	78	80	81	78	72	65	58	55	8	106	106	110	114	117	118	118	117	114	107	8
9	58	66	73	75	76	72	67	59	52	50	9	97	98	101	104	108	109	109	107	105	98	9
20	52	60	68	69	70	66	61	53	46	43	20	87	88	90	94	98	98	99	97	95	88	20
1	48	54	61	63	63	59	54	47	40	37	1	78	79	81	85	88	89	89	88	86	79	1
2	40	47	54	56	57	53	48	40	33	30	2	69	70	71	75	79	79	80	79	76	69	2
3	34	41	48	49	50	46	41	34	27	24	3	60	61	62	66	70	70	70	69	67	60	3
4	28	35	41	43	44	40	35	28	21	18	4	52	52	53	57	61	62	62	61	58	51	4
5	22	29	35	37	36	34	29	22	15	13	5	43	43	44	48	52	52	53	52	49	42	5
6	17	24	30	32	33	29	25	18	11	8	6	35	35	36	39	42	44	44	43	40	33	6
7	12	19	25	28	29	25	20	13	6	3	7	27	27	27	31	34	35	36	35	32	25	7
8	7	14	20	23	24	21	16	9	2	-1	8	18	18	18	21	25	26	26	25	13	16	8
9	3	10	16	19	20	17	12	5	-1	-4	9	9	9	9	12	16	18	17	15	13	6	9
		1	2	3	4	5	6	7	8	9			1	2	3	4	5	6	7	8	9	
30	0	7	13	17	18	15	10	3	-4	-7	30	0	-1	-1	2	5	6	7	6	3	-3	30
1	-3	4	10	14	15	12	7	0	-7	-10	1	-10	-11	-11	-9	-6	-5	-4	-5	-8	-14	1
2	-6	1	7	11	12	9	5	-3	-10	-13	2	-21	-22	-23	-21	-18	-16	-16	-17	-19	-25	2
3	-9	-2	4	8	9	6	2	-8	-13	-15	3	-33	-34	-35	-34	-32	-29	-29	-30	-32	-37	3
4	-12	-5	1	5	6	3	-1	-9	-15	-18	4	-44	-45	-46	-46	-44	-41	-41	-42	-44	-49	4
5	-15	-8	-2	2	3	0	-4	-11	-18	-21	5	-56	-57	-58	-58	-56	-54	-54	-55	-57	-61	5
6	-18	-11	-5	-1	0	-3	-7	-14	-21	-24	6	-67	-68	-69	-69	-68	-66	-65	-66	-68	-73	6
7	-21	-14	-8	-3	-2	-5	-10	-17	-24	-27	7	-78	-79	-80	-80	-79	-77	-77	-78	-80	-84	7
8	-23	-16	-10	-5	-4	-7	-12	-19	-26	-29	8	-90	-91	-92	-92	-91	-89	-89	-90	-92	-96	8
9	-26	-19	-13	-6	-7	-10	-14	-22	-29	-32	9	-101	-102	-103	-103	-102	-100	-100	-101	-104	-108	9
40	-28	-21	-15	-10	-9	-12	-16	-24	-31	-34	40	-114	-115	-116	-117	-115	-114	-114	-115	-117	-121	40
1	-31	-23	-17	-12	-11	-14	-18	-26	-33	-36	1	-126	-127	-128	-129	-127	-126	-126	-127	-129	-133	1
2	-32	-25	-19	-14	-13	-16	-20	-28	-34	-37	2	-138	-139	-141	-141	-139	-138	-138	-139	-142	-146	2
3	-34	-27	-21	-16	-15	-17	-22	-30	-36	-39	3	-152	-153	-155	-155	-154	-152	-152	-153	-156	-160	3
4	-36	-29	-23	-17	-16	-19	-24	-31	-38	-41	4	-169	-170	-172	-172	-171	-169	-169	-170	-173	-177	4
5	-38	-31	-25	-19	-18	-21	-25	-33	-40	-43	5	-177	-178	-180	-180	-179	-177	-177	-178	-181	-184	5
6	-40	-33	-26	-21	-20	-23	-27	-35	-42	-45	6	-191	-193	-195	-195	-193	-191	-191	-192	-195	-199	6
7	-41	-34	-27	-22	-21	-24	-28	-36	-43	-46	7	-204	-206	-208	-208	-206	-204	-203	-204	-208	-212	7
8	-43	-36	-29	-24	-23	-26	-30	-38	-45	-48	8	-218	-220	-223	-222	-220	-218	-216	-218	-222	-227	8
9	-45	-38	-31	-26	-25	-28	-32	-40	-47	-50	9	-233	-236	-238	-237	-235	-232	-231	-232	-236	-242	9

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Another gain is effected by recording observations in such a form that the corrections can be added directly without any copying of figures. For example, the complete record and computation for a single comparison of the bars *A* and *B* would appear about as follows:

	A	*B*
L'	3027.9	2431.9
R'	2938.1	3505.7
$L'-R'$	89.8	−1073.8
$\varDelta L-\varDelta R$	3.0	− 1.4
$L-R$	92.8	−1075.2

$$\therefore l_A-l_B=1168.0 \text{ divisions or}$$

$$=3/4 \text{ of } 1168.0 =876.0\ \mu.$$

The sum $(\Delta L - \Delta R)$ may be found mentally as the corrections are taken from the table, or the corrections may be entered separately in the record. In the above example the correction $\Delta L_A = 1.6$ is found by looking in the left half of Table 2 under 302 and interpolating for 8; similarly, $-\Delta R_A = 1.4$ is found in the right half. In the same way the table yields $\Delta L_B = 4.3$ and $-\Delta R_B = -5.7$.

Table 2 illustrates clearly the need of applying corrections, since pointings could be repeated to within a few tenths of a division. Examination of a column shows the steadily accumulating effect of progressive error and deviation of the screw from the nominal value of 3/4 μ per division. Examination of a row shows the effect of periodic error together with the slight amount of the other two errors that accumulate within one turn.

The accuracy that can be obtained in spite of such large errors is exhibited by measuring three times with each microscope the same interval of 999.05 $\mu \equiv 1332.0$ (3/4 μ). The results are recorded in Table 3, below. In each series the center of the field was located consecutively near the right edge, the center, and the left edge of the image, so as to obtain wide variations in the corrections, which were taken from Table 2. Part of the deviations from the averages are to be ascribed to inaccurate focusing and another part (perhaps) to linear interpolation, which is not altogether justifiable with such large and irregular periodic errors. Nevertheless, the agreement is even better than would have been predicted.

TABLE 3

Measurement of 999.05 $\mu = 1332.0$ (3/4 μ)

Uncorrected	Corrections		Corrected	Deviations
1341.5	−8.7	=	1332.8	+0.8
1333.1	−1.4	=	1331.7	−0.3
1337.1	−5.5	=	1331.6	−0.4
Averages with left microscope			1332.0	±0.5
1319.5	+13.1	=	1332.6	+0.5
1316.0	+15.5	=	1331.5	−0.6
1318.7	+13.6	=	1332.3	+0.2
Averages with right microscope			1332.1	±0.4

While the need of applying corrections to such microscopes as are described in Table 2 is perfectly evident, it may be well to point out in concluding this section that screw irregularities are of importance even in such micrometers as those of the International Bureau. An examination of the correction tables on pages C. xi and xii appended to Benoît's paper quoted on page 380 shows that an error of about 1.5 μ can be made in comparing two lengths if the only corrections applied are those for deviations of the mean screw-values from the nominal value of 100 μ per revolution; and further, that most of the error will be due to neglecting the *periodic* corrections.

3. DETERMINING THE CORRECTIONS OF MICROMETER MICROSCOPES

The calibration of a microscope by one of the processes usually described involves such laborious computations and least-square adjustments that it is no wonder to find it attempted only as a last resort when the demands of high accuracy compel. While, of course, the complete calibration of any divided scale requires considerable time, it is, however, possible to determine microscope corrections more accurately and with less labor than would appear from previous accounts. The whole procedure can be made one of direct measurement and simple graphical addition.

In determining the screw errors it is customary to use the ocular of the microscope under investigation for viewing the displacements of the spider lines. An enormous gain, however, is secured by removing the ocular and measuring the displacements by means of a second micrometer microscope.[10] The micrometer box may be detached from the microscope tube and mounted on the carriage of a dividing engine or other apparatus convenient for producing relative motion between the micrometer and the auxiliary microscope; but the writer prefers to remove the ocular only. The spider lines may be agreeably illuminated by placing beyond the objective a piece of milk glass or of thin white paper, behind which is mounted a small incandescent electric light. The auxiliary microscope is held by a slide that affords smooth motion in three directions mutually perpendicular.

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[10] The use of an auxiliary microscope for this purpose was first brought to my attention by Mr. Tillyer, who informed me that it was the regular practice at the United States Naval Observatory. (See J. C. Hammond: "Introduction to publications of U. S. Nav. Obs.," 6, Axiii.; 1911.) Sir David Gill (Roy. Astron. Soc. Monthly Notices, 45, p. 65; 1884) also employed a compound microscope in a simple apparatus he designed for rapidly and accurately investigating screw errors; but his method is in several respects inferior to that of the Naval Observatory.

We now measure: (1) The distance traveled by the spider lines as the screw under investigation is advanced five whole turns (a different number of turns may sometimes be more convenient); (2) the distance traveled during each single turn; (3) the distance traveled during each fifth (or tenth) of a turn. It is not necessary that the screw of the auxiliary microscope be very accurate, because all the pointings will be confined to the same portions of this screw, each only a fraction of a turn long. Besides, any irregularities here will be rendered negligible by choosing an objective that will magnify the interval to be measured sufficiently to make its image nearly fill the usable portion of the field of view. It is not necessary to use the same objective in measuring all three intervals, though it may be more convenient to do so. In obtaining the data for deriving Table 2 a 1-inch objective was used for the five-turn intervals, and a one-half-inch objective for the other intervals. All the lengths were then expressed in terms of the same unit, namely, one-drum division of the auxiliary microscope with the one-half-inch objective. The measurement of consecutive five-turn intervals for the entire length of the screw is not necessary, but it is advisable in order to reduce the accumulation of errors by addition in determining the progressive corrections; and the extra time consumed is a small item. Again, it is hardly worth while to carry out measurements (2) and (3) with every turn. It will usually be found sufficient to measure the first and the last turn of each five-turn interval. Since adjacent turns are not likely to differ much, this grouping in pairs will check blunders.

In measuring an interval the following procedure is observed: The auxiliary microscope (which we shall designate by A) is first focused on a transverse spider line attached to the screw (S) to be examined, and the image of this spider line is made parallel with the spider lines of A, care being taken to use always the same place of the observed line, preferably close to the longitudinal line. S is now set accurately at the beginning of the interval to be measured, using for this purpose a lens to note coincidence between the line on the drum and that on the index. A is now pointed on the spider line of S and the reading is recorded. Then S is turned to the end of the interval and two pointings of A made. As a check against accidental displacements, S is returned to the beginning of the interval and the pointing of A repeated. The sensitiveness of the method is such that discrepancies exceeding the accidental error of a pointing can usually be traced to failure in setting S with sufficient accuracy at the boundaries of the interval. It is hardly worth while to increase the precision by averaging more than two pointings at each end. After measuring one interval, the screw S is advanced to the beginning of the next. Then the slide carrying A is moved until the spider line of S is again pointed at (the micrometer of A always being set to read the same at the beginning of each interval), and the procedure described for the first interval is repeated. When intervals of a different length are to be measured, the initial setting of A is so chosen that the same narrowly restricted portion of its screw will be used in pointing at the ends of all intervals. The pointings at the beginnings need not vary more than a few hundredths of a turn for all the intervals of approximately the same length.

After all the intervals have been measured, a length close to the average for one turn of S is selected as a basis of comparison. A multiple of 10 divisions of A is convenient. By simply adding the deviations of the measured five-turn intervals from five times this basis, we compute the progressive corrections at the beginning of each five turns, choosing the point of zero correction at the middle of the screw. These corrections will be expressed in divisions of A, and the same unit is retained in all stages of the computation until the end, when the correction curves are read off by a scale which automatically translates into the numbers to be entered in the final table.

We now plot a series of curves the abscissæ of which are the whole turns of S—that is, the comb readings of the micrometer to which it belongs. Figure 2 is a reproduction of those used in computing Table 2. The ordinates of the first curve (C$_0$), measured from the dash dot line M N corresponding to 1170 divisions of A, are the progressive corrections mentioned in the preceding paragraph; those of the second (C$_{100}$) are the lengths of the one-turn intervals; those of the next five ($_0p_{20}$, $_{20}p_{40}$, $_{40}p_{60}$, $_{60}p_{80}$, $_{80}p_{100}$) are the lengths of the one-fifth turn intervals in proper order. The next step is to adjust these curves so that they are mutually consistent; that is to say, the progressive corrections found by adding five consecutive ordinates of C$_{100}$ measured from M N should agree with the corrections represented by C$_0$, and any ordinate of C$_{100}$ should equal the sum of the corresponding ordinates of the curves $_0p_{20}$ . . . . . $_{80}p_{100}$. If the curves are plotted to a suitable scale, the

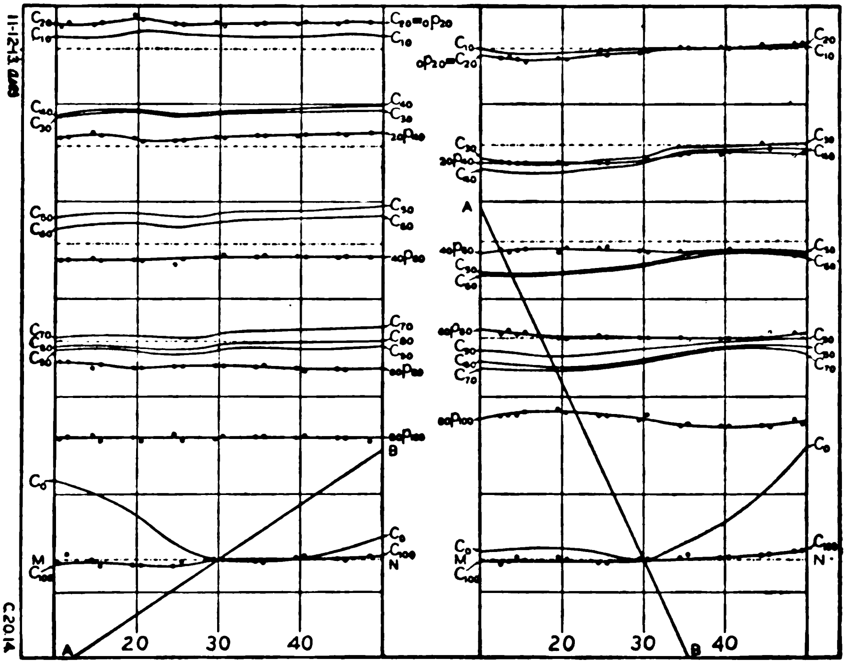

Fig. 2.—*Curves showing the corrections of a pair of micrometer microscopes used on a transverse comparator. The distance separating the light horizontal lines corresponds to a correction of 0.0513 turn, or 3.85 microns*

additions are quickly made by marking off the distances on strips of paper. These adjusted curves afford a fairly safe means of interpolation to obtain the corrections for intervals not actually measured. The curve plotted from the sums of the components of each interval is likely to lie above or below that plotted directly from the entire intervals. This divergence can proceed from progressive error or gradual change of scale-value in the screw of the auxiliary microscope or from thermal expansion of S, but it is of no consequence. The adjustment is first directed toward rendering the two curves parallel; then any distance separating them is divided among the curves representing the components of the interval by merely shifting the base lines from which the deviations would be measured. A small amount of such divergence was distributed among the curves for the right microscope.[11]

After the adjustments have been completed, the curves for the one-fifth turn intervals are added graphically to form a new set (C_{20}, C_{40}, C_{60}, C_{80}) yielding the corrections at the beginning of each fifth by measuring ordinates from the dash-dot lines corresponding to 1/5 of 1170 = 234 divisions of A. If interpolation is necessary, it is readily accomplished graphically with sufficient accuracy. The interpolating curve for any selected turn will exhibit the corrections at every drum reading within this turn. Five points beside the initial zero are obtained from the correction curves just mentioned. If interpolating curves are plotted for several turns evenly distributed along the course of the screw (Fig. 3), sufficient data can be obtained for plotting curves (C_{10}, C_{30}, C_{50}, C_{70}, C_{90} of Fig. 2), to give the corrections at every tenth of a turn, or oftener, as functions of the comb readings. All that now remains is to determine the magnification and to translate these curves into the figures that form the final table.

It is, of course, desirable that the numbers in the correction table, and also the tabular differences, be small. Tabular differences arising from periodic irregularities can not be reduced except by improving the screw. Progressive errors and deviations from the nominal screw-value, however, even if small, lead to the accumulation of large corrections when many turns must be used. But if the magnification is adjustable, these corrections can often be materially reduced. The first of the series of curves plotted, namely, that representing the progressive errors, was based on deviations of the measured lengths of individual turns from the length represented by the basis selected for comparison. If a known length, such as a standard millimeter, be measured with the microscope to which the screw S belongs, and the readings corrected by using the curves described above, the distance measured that would correspond to the basis of comparison is likely to

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[11] Although adjustments of this kind made by different computers would probably differ slightly, a least-square solution would be a sheer waste of effort, since the differences in almost any case would affect the final corrections by considerably less than the accidental error of a pointing in using the micrometer of which S forms a part.

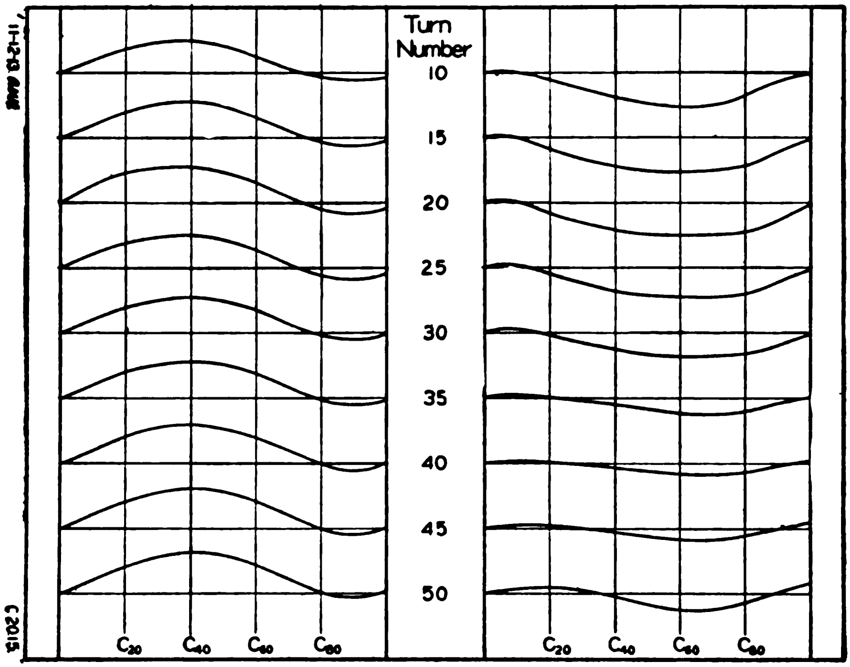

Fig. 3.—*Interpolation curves showing the corrections necessitated by periodic errors in the micrometer screws. The distance separating the light horizontal lines corresponds to a correction of 0.0342 turn, or 2.56 microns*

differ somewhat from the distance to be represented by 100 divisions (one turn) in the correction table. A little reflection will make it apparent that corrections for this divergence can be added to the progressive corrections by the simple device of drawing a line (AB) at the proper angle through the point selected for zero correction. The distance parallel to the axis of ordinates between this line and the progressive curve (C_0) measures the total correction for any comb reading. It is, therefore, evident that these corrections can be reduced to a minimum for any given part of the screw by adjusting the magnification of the microscope so as to give this line the most favorable slope. A moment's inspection of the progressive curve will decide what this should be. After the magnification has been adjusted with sufficient closeness, a standard length interval should be carefully measured, and the correcting line accurately located. Several measurements using different parts of the screw will afford valuable checks on the accuracy of the correction curves. Table 3 above represents measurements of this kind.

We are now ready for the final step of reading off the corrections from the curves and entering them in the table. A translating scale is used which reads the plots in terms of the unit chosen for expressing the corrections in the table. A piece of coordinate paper cut diagonally at the proper angle forms a convenient scale. The corrections at the beginning of each turn are measured by the distances between the curve of progressive corrections and the inclined line correcting for magnification. The corrections at the tenths of a turn are read from the corresponding curves, the base line of each being shifted if necessary to correct for magnification within a turn. (Progressive errors within a turn as well as periodic errors were cared for in deriving the curves.) These internal corrections must, of course, be added to the correction at the beginning of the turn before entering in the table.

WASHINGTON, November 5, 1913.

THE PENTANE LAMP AS A WORKING STANDARD

By E. C. Crittenden and A. H. Taylor

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I. INTRODUCTION

1. PURPOSE OF PAPER

In the Transactions of the Illuminating Engineering Society there have already been published two papers [1] dealing with the work on flame standards of candlepower which has been done at the Bureau of Standards. These papers were intended to be particularly reports of progress in the experimental work which has been done on various types of lamps. The investigation of the lamps was made with the double purpose of determining whether any of them were capable of furnishing a check on a possible drift in the value of the unit now maintained by electric incandescent standards, and of finding a satisfactory working standard for use where electric standards are impracticable.

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[1] Trans. Ill. Eng. Soc., 5, pp. 753–778, 1910; and 6, pp. 417–432; 1911.

The results of that work proved to be distinctly favorable to the use of the Harcourt 10-candle pentane lamp as a secondary standard. Since the publication of the papers mentioned the use of such lamps has become much more extensive, and the present paper is written with a somewhat different object in view, namely, to cover the questions which have arisen regarding their operation. This involves a fullness of detail which may not be of much interest to the general reader, but which it nevertheless appears desirable to put in print because some of this information is not generally available. Directions for the use of these lamps in making tests of gas are issued by the Metropolitan Gas Referees of London, who developed this type of lamp. Their directions, however, are not entirely applicable to American practice, and in some respects the methods here described differ materially from theirs.

2. EXTENT OF USE OF PENTANE LAMPS

The number of pentane lamps tested by the Bureau is not an exact indication of the extent to which the use of the lamps has increased, because many have been standardized in other laboratories and many others, especially in the early years of their use, were not standardized at all. Nevertheless, the number tested by the Bureau as given in the statement below, is an indication of the widespread adoption of this standard.

1908	4	1912	35
1909	6	1913 (6 months)	15
1910	7	Total	84
1911	17		

Since in many cases one of these lamps furnishes the basis on which the quality of the gas supply of a city, so far as candlepower is concerned, is judged, the importance of the pentane lamp in present practice will be appreciated.

While the lamp has found its widest use in gas testing, where a flame standard is preferred because the effects of atmospheric conditions on it compensate for similar effects on the gas flame, its usefulness is by no means limited to work of that kind. The corrections to determine the actual candlepower are easily made, and the lamp affords a fairly convenient method of obtaining a basic standard for laboratories which lack the batteries and accurate instruments which are necessary to get dependable values from electric standards.

In some cases the pentane lamp may thus serve as a basis of standardization even when it may be found more convenient to use other working standards for the actual tests. For example, when a series of measurements are made extending over several hours another source, such as a kerosene lamp, an Edgerton standard, or a gas mantle may be used as a constant comparison light at one end of the bar, its value being fixed by substituting a pentane lamp for the test flame or lamp at the beginning and the end of the series. An electric lamp kept at constant current may be used in the same way as a comparison light. This is exactly what is done in most portable photometers, and the calibration of such photometers can be based on a pentane lamp as well as on an electric standard. A modification of this practice, which is useful where tests for approximate values have to be made at a number of stations, is to provide for each station a portable standard unit consisting of a low-voltage lamp and a storage battery, the whole unit being brought in at regular intervals for recharging and recalibrating against the pentane standard. From a curve showing the variation in candlepower with time of use for such a unit one can obtain fairly satisfactory values without the use of either regulating resistances or electrical measuring instruments. The details of such a system in actual operation have recently been described.[2] In using such standards, as in any case where electric lamps are compared with flames, the effects of humidity are important. The readings can, however, be easily corrected for this by the use of such a chart as is given in Fig. 3.

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[2] H. L. Farrar: Gas Age, **31**, pp. 407–409 (Apr. 15); 1913.

It is hardly necessary to give here a long discussion of the relative advantages of different lamps and of the reasons which are leading to the common use of the pentane lamp as a working standard in this country. There are other lamps which may be used in cases where their value can be frequently checked or where the accuracy required is not great. In some other cases, especially where portability is an important consideration, the Hefner lamp is to be recommended; by making many measurements under favorable conditions very good results can be obtained with it, but in general its low candlepower, comparatively red light, extreme sensitiveness to drafts, and unsteadiness at temperatures above 70° F. make it difficult to use. The pentane lamp has the disadvantages of being large and not easily portable, of using fuel which is expensive and somewhat dangerous, and of requiring more air than ordinary ventilation will supply. In spite of these faults its use is increasing, chiefly because it appears to be the only standard of candlepower now in use, other than incandescent electric lamps, which can be relied upon to give, under the usual working conditions, the degree of accuracy expected in present commercial practice.

II. STANDARDIZATION OF LAMPS

1. NECESSITY OF PHOTOMETRIC TEST

The necessity for standardization of each lamp by a photometric test arises from the fact that different lamps, even of the same maker and supposedly of the same type, show differences in candlepower which are sometimes as great as 4 per cent. The construction is such as to make it difficult to determine after a lamp is assembled whether it is built exactly according to specifications. In fact, exact adherence to specified dimensions might not remove the differences between lamps unless other conditions also were definitely specified. For example, the castings used in the American lamps have a rough inner surface; this roughness probably facilitates the transfer of heat to or from the air, and it may also affect slightly the flow of air through the passages. Whatever may be the cause of the differences between lamps, the candlepower of the individual lamp is the important thing, and the logical test is to determine the candlepower. In lamps tested at the Bureau details of construction are not given special attention unless some part is so made that it appears to be a possible cause of variation in the candlepower of the lamp.

Since the lamp itself is only an instrument for producing the actual standard, the flame, there is little significance in a value given for the lamp unless other factors, such as air and fuel, and other conditions of operation are known. The value certified for a lamp applies strictly only for its use under conditions identical with those under which it was standardized; it may, therefore, be worth while to particularize rather fully the method of testing followed at the Bureau.

2. PHOTOMETER ROOM—VENTILATION, SCREENING, AND APPARATUS

The photometer room used hitherto is approximately 26 by 18 by 12 feet. Ventilation is obtained by a tempered air heating system. The ordinary ventilation would not keep the air sufficiently pure if the flame gases were allowed to escape into the room, and consequently above the lamp is hung a hood 2 feet in diameter, with an outlet into one of the ventilating ducts. The draft into this hood is just strong enough to insure that all the gases rising from the lamp shall pass into the hood and thus be carried out of the room. This arrangement is so effective that no perceptible change in the candlepower of the lamps due to vitiation of the air occurs in several hours' continual burning. In regular work, however, the room is usually aired out at least once every hour.

The photometer room is in a corner of the building and often has troublesome drafts, in consequence of which it has been found that the performance of the lamps has been improved by screening them on three sides and sometimes on all four sides. This is done by a wooden framework about 3 feet long, 2 feet wide, and 3 feet high, carrying a strip of cloth which extends from the top of the frame down to 6 inches from the bottom, thus allowing free access of the air from all sides below the lamp but preventing any drafts from striking the flame or the circulatory system of the lamp directly. This screening was adopted after many trials of various forms of inclosure had shown that in most of them the lamps gave values slightly different from those obtained in the open, even when no vitiation of the air in the inclosure could be detected.

In special tests of the state of the air a Zeiss refractometer has been used to determine the quantity of CO_2 present. Measurements of atmospheric moisture are regularly made with two Assmann psychrometers, and of pressure by a mercury barometer. The details of the calculation of the moisture will be given later, in connection with the corresponding corrections.

The photometer outfit is of the standard form regularly used at the Bureau, with Lummer-Brodhun contrast head and a recording device of which a description has been published.[8] The substitution method with constant intensity on the disk is used as in all standard work—that is, a constant "comparison lamp" is connected to the photometer head at a fixed distance from it, while the electric "working standards" and the pentane lamps under test are alternately put in on the other side for reading.

3. ADJUSTMENT OF LAMPS

Before putting the lamp on the photometer the chimney is inspected by looking down through it to see that it is set centrally over the burner, and each time the lamp is lighted the gauge is applied to make sure that the chimney is at the proper height—that is, 47 mm above the burner when cold. The chimney seldom has to be reset, but occasionally one creeps slightly with heating and cooling.

In setting up the lamp on the table care is taken to level it so that the chimney shall be vertical. The levels (plumb bobs on later lamps) attached for this purpose are not always exact, and this leveling is done by dropping a plumb line from the center of the top of the chimney, so that the bob should hang centrally in the burner. The height of the lamp is so adjusted that the middle of the flame is on a level with the center of the photometer disk. The directions of the Gas Referees are such as to bring the bottom of the chimney on a level with the center of the disk, and this setting makes the illumination on the disk follow the inverse square law more exactly than if the lamp is higher. The American Gas Institute's committee on taking candlepower of gas has, however, recommended the other position, and in order to avoid confusion the Bureau has followed this recommendation. The lamp is usually placed so that the axis of the photometer passes through the air tube as well as through the center of the burner and chimney. In some cases, however, on request, the lamps are turned 90°, so that a plane passing through the chimney and the air tube is at right angles to the photometric axis. No difference has been detected in the values obtained in the two positions for any lamp. In either case the chimney is so turned that the light from the mica window does not fall on the photometer disk or on the lamp standard or the pentane feed tube.

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[8] G. W. Middlekauff, this Bulletin, 7, p. 18, 1910; and Elect. World, 56, p. 153, (July 21); 1910.

In measuring distances from the lamp the center of the burner is taken as the point of departure. The photometric observations are made at a distance of approximately 1 meter. For setting the lamp at the proper point on the scale it has been found convenient to follow the English method of using a rod having near one end a cylindrical plug which fits into the burner. This rod is made of such length that the other end just touches the photometer head when the center of the burner is 1 meter from the disk. This fixes very exactly the point of the scale which is 1 meter from the lamp, and a line on the record sheet is set at this point. The distance of the comparison lamp is then so chosen as to make the settings on the pentane lamp fall near the line, and in working up the sheet the distances of the groups of points which represent readings on the lamp are measured from this line.

4. OPERATION OF LAMPS: PENTANE, FLAME HEIGHT, AND TIME OF BURNING

The pentane used is tested with respect to density and purity; the effects of possible variation in the fuel are so important that a later section of this paper is devoted particularly to that question.

The method of controlling the flame height has been the subject of considerable difference of opinion. At the Bureau no difference in candlepower has been found to result from the use of the various cocks at which regulation may be effected. Even when the saturator is entirely closed off from the air, and the pressure of the vapor in it is allowed to run up to 9 inches of water, regulation of the flame height being made by a cock near the burner, no departure as great as 1 per cent from the normal candlepower occurs. In standardizing the older lamps, in which such cocks are provided, they have been used. The newer lamps do not have these cocks, and flame height is controlled by the outlet cock of the saturator, in which case greater ease of adjustment is obtained by clamping a lever on to the handle of the cock.

Another question concerning which there are differences of opinion is that of the proper flame height. In English lamps the top of the flame should be set at the middle of the lower mica window, about 27 mm above the bottom of the chimney. The lamps are so proportioned that with this height of flame the candlepower is near its maximum, and a small shift up or down makes very little change in candlepower. This is shown in curve E of Fig. 1, where abscissas are candlepowers and ordinates are heights of flame in the chimney. The effect of personal error in judgment of height of flame is thus made very small.

The American makers have placed the crossbar of the window lower, and direct that the flame be set with the tips at the top of the bar, which is about 22 mm above the bottom of the chimney. As is shown in curve A of Fig. 1, this is not high enough to give the maximum candlepower, and at this height small changes cause relatively large variation of candlepower.

At the Bureau it has been considered important to retain the advantage given by using the maximum candlepower, and incidentally to adhere to the original manner of operating the lamps. The practice has therefore been definitely adopted of first determining the height of flame which gives the maximum candlepower for a given lamp, and then standardizing the lamp with the flame at that height. With American lamps the maximum is usually obtained when the top of the flame is nearly a centimeter above the bar. A line is marked on the window to show the height used, and the fact is stated in the certificate furnished with the lamp. The candlepower thus obtained is usually from one-half per cent to 1 per cent higher than would be given if the flame were set to the top of the bar.

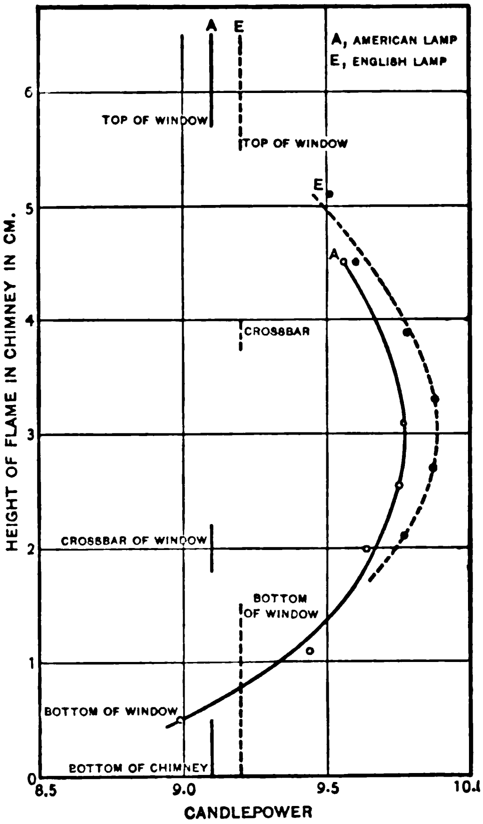

Fig. 1.—*Variation of candlepower of pentane lamps with height of flame*

The necessity of waiting a sufficient time after lighting the lamps before making measurements was emphasized in the earlier papers, where curves were given showing the variation of candlepower with time after lighting for English and American lamps. It is important to note that the candlepower rises rapidly at first, going above the normal, and then settles back to a fairly constant value. Considerable attention has been given to the measurement of the variations in temperature in various parts of the lamp which accompany these changes in candlepower. The details of the measurements will not be given here, but it may be said that they have strengthened the conviction that most of the change in candlepower caused by variation in conditions of operation may be attributed to the air circulating system and the variations in the flow of air which arise from changes in the relative temperatures of parts of the lamp. There is a slow change of temperature for a considerably longer time, but the candlepower is practically constant after 30 minutes in the case of the old style American lamps and after 20 minutes with the newer lamps. The excess of the maximum over the final candlepower is about 3 per cent and 2 per cent, respectively, for the two types. Lamps of the English type run from 1 per cent to 1½ per cent high at the maximum and may be considered constant after 15 minutes burning. The smaller heat capacity of these lighter lamps, which allows them to reach a steady state sooner, seems also to make them more susceptible to variations caused by changing drafts.

5. BASIS OF STANDARDIZATION

The fundamental unit in terms of which lamps are certified is the international candle[4] as maintained by the primary electric standards of the Bureau. The standards actually used in tests are a group of seven carbon lamps operated at low voltage so as to match the pentane in color. Since the flame is much redder than the ordinary electric standards the calibration of these special standards has taken considerable labor to insure that no important error be introduced because of this color difference. The group has been compared with the Bureau's regular working standards in three series of measurements by a number of different observers, under the direction of Dr. Middlekauff, and the average values have been as follows:

	Candlepower
1911	4.98
1912	4.98
1913	4.97

It appears therefore that the uncertainty in the value of these standards can not be very great. As a check on their permanence another group carefully compared with them is preserved and used only for checking the working standards. A similar group has also been prepared to be sent to England in order to obtain a direct comparison between the standards of the National Physical Laboratory and those of the Bureau operated at the color of the pentane flame.

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[4] Bureau of Standards Circular No. 15.

To obtain the normal candlepower of the flame corrections are made for the effects of atmospheric moisture and pressure. These corrections will be considered in a separate section, since they must be used whenever it is desired to obtain absolute candlepower values with a flame standard. As a check against the introduction of errors by other conditions, such as poor ventilation, which might affect the flames but not the electric standards, a pentane lamp of known candlepower is always included in test runs.

6. NUMBER OF MEASUREMENTS

The number of measurements made on each test lamp in the course of standardization depends somewhat on the consistency of the results obtained. Usually each lamp is placed on the photometer about six times, and each time 4 measurements are made, each consisting of 25 to 40 settings of the photometer. The candlepower for each measurement is worked up separately, and if the average deviation of these values from the final mean is not materially greater than one-half per cent, and the values obtained for the check lamp run in the test are also normal, the test is considered satisfactory. If these conditions are not fulfilled, further measurements are made until it is believed that the mean candlepower of the lamp is sufficiently well determined. The candlepower is certified to the nearest tenth of a candle unless the average of test results falls very nearly halfway between tenths, in which case a subscript 5 is given in the hundredths place; this is written as a subscript to indicate that it is considered not as definitely established but merely as representing the average of test results.

7. ACCURACY OF VALUES

With all the precautions taken it is believed that the values certified for the lamp are correct within 1 per cent; that is, that under similar conditions the lamps should give average results within 1 per cent of those certified. It has occasionally happened that a second test on a lamp has given a result fully 1 per cent different from the value originally certified. The result obtained from a single time on the photometer sometimes departs as much as 2 per cent from the mean, but the maximum deviation is seldom as great as this. As for the permanence of the calibration no evidence has been obtained indicating any appreciable change with time. For the Bureau's two Chance lamps, which are regularly used as checks on tests, the average candlepowers found in 1910 were 9.87 and 9.89; the averages for the first six months of 1913 have been 9.90 and 9.87.

Conditions in different laboratories are not likely to be exactly the same, and in order to depend on reproducing values in different places as closely as 1 per cent one would probably need to give some care to reproducing conditions of operation. It would seem, however, that under any reasonably good conditions the difference ought to be well within 2 per cent, for, using good pentane and correcting for atmospheric moisture and pressure, it is difficult to produce that much variation in candlepower by any intentional change of conditions except vitiation of the air or incorrect flame height.

III. GENERAL DIRECTIONS FOR USE OF PENTANE LAMPS

It is hardly practicable to give here detailed directions as to the exact procedure to be followed in any case, but attention may be called in a general way to some precautions which should be taken in using the lamps. Many of the details of adjustment and operation which have already been discussed will be merely mentioned here. The best results will presumably be obtained by following the same methods in operating a lamp as were used in standardizing it. If the lamp to be used has been standardized at the Bureau, a reference to the preceding pages will answer most questions as to proper procedure. If the value of the lamp has been assigned by another laboratory, such questions should usually be referred to that laboratory.

I. VENTILATION AND EFFECTS OF VITIATION OF AIR

Since all flames depend upon combustion it is to be expected that their intensity will vary with the proportion of oxygen and of other constituents in the air supplied to the gaseous fuel of the flame. To maintain a flame in a constant condition requires, therefore, not only uniform fuel, but also a uniform proportion of oxygen in the air supplied to the flame. Good ventilation is consequently desirable for all work with flames, and is indispensable where lamps of other kinds are to be compared with a flame standard. The quantity of air which must be supplied depends largely on the size and number of flames in the room and also on the method of ventilating. The flames themselves set up currents of air, and if possible these currents should be utilized to remove immediately from the room all the vitiated air coming from the lamps. A hood placed above the photometer with a rising pipe to lead the warm air out of the room is most effective.

If the gases from the flames are allowed to diffuse into the room and are simply diluted by the air entering, a much larger amount of fresh air will be needed. In such a case it has been estimated [5] that to keep the carbon dioxide content of the air down to 6 parts in 10 000, 3000 cubic feet of fresh air per hour must be supplied for each person in a room. A committee of the American Gas Institute [6] has on this basis estimated that 36 900 cubic feet of air per hour should be supplied for a photometer room where two persons work with a pentane lamp and a 5-foot gas flame, since in the production of carbon dioxide the gas flame is approximately equivalent to six persons and the pentane lamp to four.

In a room where air enters at the bottom and escapes at or near the top the quantity estimated as above (about 12 000 cubic feet per hour for a pentane lamp) is probably ample for any purpose, and if care is taken to allow direct escape of the flame gases a much smaller amount is sufficient.

Some caution is necessary in making calculations based on the quantity of carbon dioxide in the air. Experimental determinations of the effect on flames have sometimes been made by adding carbon dioxide to the air, and it must be remembered that the dilution of the air by a quantity of added CO_2 has relatively little effect as compared with the conditions arising when the same amount is formed in the process of combustion, using up the oxygen of the air. In the formation of 5 cubic feet of CO_2 by the combustion of pentane, for example, 8 cubic feet of oxygen are used. Since the abstraction of 1 cubic foot of oxygen has practically the same effect on the composition of the air as the addition of 5 cubic feet of inert gas, it is evident that the reduction in the amount of the active oxygen is of much greater importance than the increase in the diluting gases. The effect produced on the Hefner lamp by adding 1 part of CO_2 to 1000 of air, according to Liebenthal,[7] is a reduction of 0.7 per cent in the candlepower, but the generation of the same proportion of CO_2 by combustion and breathing in a room has been found [8] to be accompanied by a decrease of 2.2 to 3 per cent in the Hefner, the pentane lamp, and other flames. In general, the effect depends on the manner of production of the CO_2, since the greater part of the decrease is due not to the presence of CO_2 but to a deficiency of oxygen. Determinations of the amount of CO_2 in the air, consequently, do not furnish sufficient data for exact correction for vitiation of the air, but are useful in that they enable one to judge the effectiveness of the ventilation.

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[5] Kent: Mech. Eng. Pocketbook, 1912 ed., p. 654. [6] Proc. Amer. Gas Inst., 2, pp. 481–482; 1907.

In many cases, however, determinations of CO_2 are not practicable and the effectiveness of the ventilation must be judged by other means. When facilities are available for setting an electric lamp repeatedly to the same current a direct test can be obtained by making a series of measurements of the electric lamp against the pentane and finding whether the latter shows a gradual decrease after it should have reached a constant value. Another test which is as definite as determination of the carbon dioxide and far more easily carried out is afforded by careful measurement of the humidity, for the processes which use up oxygen add water as well as CO_2 to the air. If the water vapor regularly increases by an appreciable amount during the operation of the lamp, the ventilation is not satisfactory. An increase of 1 liter of water vapor per cubic meter of air, when caused by poor ventilation, is quite regularly accompanied by such vitiation as to cause about 2 per cent decrease in the candlepower of flames, in addition to the 0.6 per cent decrease caused by the water vapor itself.

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[7] Zs. f. Instrumentenkunde, **15**, p. 157; 1895.

[8] C. C. Paterson, Collected Researches, National Phys. Lab., **8**, p. 49; 1908. Butterfield, Haldane, and Trotter, Jour. Gas Light, **115**, p. 290, 1911, and Amer. Gas Light Jour., **95**, p. 145, 1911; also unpublished tests of Bureau of Standards.

In designing ventilating inlets ample capacity should be provided to allow a slow flow of air into the room in order to avoid drafts which would cause unsteadiness of the flame. Similarly, if a hood is used as recommended, the outlet must be so arranged that the flow of air into the hood shall not be too vigorous. Troublesome drafts are apt to arise if the walls of the photometer room differ much in temperature from the air. It is therefore desirable that none of them shall be exterior walls of the building. If such walls are unavoidable, they should be either jacketed with nonconducting material or covered by a false wall with an air space. If possible, the room should be so free from drafts that the flame will burn steadily without other protection than the necessary photometric screens. If further protection from drafts is necessary, a screen of the form described on page 395 should be used.

2. PREPARATION OF LAMP

In preparing the lamp for use one should observe the following details: Centering of chimney over the burner, height of the chimney above the burner, direction in which the mica window is turned, amount of pentane in the saturator, height, orientation, and leveling of the lamp, and its distance from the middle point of the bar or some other definite point on the scale. It is advisable, at least in the beginning, to check the last two adjustments by direct measurement, as described on pages 396 and 397. If then the plumb bobs (or the level and bob) are found to be correct, they may be used thereafter.

The saturator should be from one-third to two-thirds full of pentane at starting, and the height of the liquid as seen against the window of the saturator should never be less than 3 mm (one-eighth of an inch). Since pentane is very volatile and inflammable, and the heavy vapor flows downward, it is extremely hazardous to fill a lamp while it is burning. This should never be attempted under any circumstances, and it should be an inviolable rule of the laboratory that no pentane in an open vessel be brought near any flame.

Immediately before the lamp is lighted the height of the chimney should always be tested with the gauge, and occasionally the gauge itself should be measured to see that it remains 47 mm long.

3. OPERATION

To light the lamp open first the saturator inlet cock, then holding a lighted match over the burner open the outlet cock gradually. If the lamp has a regulating cock near the burner, the saturator cocks may both be opened and the flame controlled by this regulating cock. If no such cock is provided, the saturator outlet cock is used for regulation. Usually on opening the cocks the vapor will flow so that the lamp will light, but it is sometimes necessary to start the flow of vapor by blowing gently into the saturator inlet. Sometimes also the lamp at first burns with a small blue flame because the heavy vapor has flowed down into the burner and prevents the normal circulation of air from starting. If this happens, shut off the cocks, and blow up into the outer chimney to start the air, keeping below the burner to avoid the small burst of flame which may result if the flame has not entirely died out in the tip. The lamp will then light normally. After it is lighted see that the conical hood around the flame is so placed that the whole flame is visible from the photometer disk.

The flame should be kept at approximately the correct height, and no measurements should be made until the lamp has burned 15, 20, or 30 minutes, according to whether it is of the English type or of the new or old American forms. Unless otherwise specifically stated in the lamp certificate for the American lamps the proper flame height is obtained when the tips are just above the crossbar of the window, while in English lamps the flame should extend halfway up the lower window. As already stated, American lamps standardized recently at the Bureau of Standards have a line on the window to which the top of the flame is to be set. After the lamp has burned a few minutes such changes in flame height as occur are gradual, and except in the most careful work it is not necessary to have a special observer to watch the flame.

The lamp is extinguished by shutting off the saturator cocks. When it is not in use both cocks should be kept closed, and a cap should be placed over the burner to prevent injury to it or the collection of dust in the passages. All parts of the lamp should be kept well blackened.

IV. PENTANE—PREPARATION, TESTING, AND USE

1. PREPARATION AND TESTING

The directions of the Gas Referees for the preparation and testing of pentane are as follows:

> *Preparation.*—Light American petroleum, such as is known as Gasoline and used for making air-gas, is to be further rectified by three distillations, at 55° C., 50°, and 45°, in succession. The distillate at 45° is to be shaken up from time to time during two periods of not less than three hours each with one-tenth its bulk of (1) strong sulphuric acid, (2) solution of caustic soda. After these treatments it is to be again distilled, and that portion is to be collected for use which comes over between the temperatures of 25° and 40°. It will consist chiefly of pentane, together with small quantities of lower and higher homologues whose presence does not affect the light of the lamp.
>
> *Testing.*—The density of the liquid pentane at 15° C. should not be less than 0.6235 nor more than 0.626 as compared with that of water of maximum density. The density of the pentane when gaseous, as compared with that of hydrogen at the same temperature and under the same pressure, may be taken. This is done most readily and exactly by Gay Lussac's method, under a pressure of about half an atmosphere and at temperatures between 25° and 35°. The density of gaseous pentane should lie between 36 and 38.
>
> Any admixture with pentane of hydrocarbons belonging to other groups and having a higher photogenic value, such as benzene or amylene, must be avoided. Their presence may be detected by the following test: Bring into a stoppered 4-ounce bottle of white glass 10 cc of nitric acid, specific gravity 1.32 (made by diluting pure nitric acid with half its bulk of water); add 1 cc of a dilute solution of potassium permanganate, containing 0.1 gram of permanganate in 200 cc. Pour into the bottle 50 cc of the sample of pentane, and shake strongly during five successive periods of 20 seconds. If no hydrocarbons other than paraffins are present, the pink colour, though somewhat paler, will still be distinct; if there is an admixture of as much as one-half per cent of amylene or benzene, the colour will have disappeared.

For the benefit of those who are not chemists it should be said that this last test should always be preceded by a blank test to check the purity of the reagents, for if the nitric acid is not pure it will decolorize the permanganate. The acid should be kept in the dark to avoid deterioration.

The pentane used at the Bureau is tested with respect to purity and density of the liquid. The density is conveniently determined by a hydrometer carrying a thermometer. The correction for temperature is important, being about 0.001 per degree centigrade or 0.00055 per degree Fahrenheit.

2. CHANGE DURING USE, AND CORRECTION DETERMINED BY DENSITY

In the sealed ether cans in which pentane is now purchased no difficulty has been found in keeping a supply which fulfills the specifications when the cans are opened, but the more rapid evaporation of the lighter fractions raises the density as the fuel is consumed in the lamp. It is quite impracticable to work with pentane within the limits prescribed, for the density is certain to be too high before one-tenth of the pentane is consumed; in fact, the density usually reaches 0.635 when a little over half has been used.

The directions of the London Gas Referees are to empty the saturator completely at least once a month when three tests daily are made, but this appears to be decidedly too long a period. The residue of higher density gives a slightly higher candlepower than the fresh pentane. When repeated additions of fresh fuel are made, and the accumulated residue remains in the lamp, a mixture is obtained such that an appreciable change in candlepower may occur in a relatively short time. It therefore appears desirable to empty the saturator after it has been replenished only three or four times. It is not necessary, however, to discard the portions emptied out; if these are collected and not mixed with fresh pentane, fairly reliable results can be obtained by using the residues thus collected, making a suitable correction determined by the density. Considerable attention has been given to the determination of such a correction, and the results of the measurements made are shown in Fig. 2. The relation between candlepower and density is probably not really linear, but for present purposes may be assumed so. It will be seen that the change in candlepower averages about 1 per cent for an increase of 0.01 in the density of the fuel. Samples of pentane from different sources which have been initially high in density have also given results agreeing fairly well with this rule. Consequently, it appears to be allowable to apply such corrections in many cases where the expense for pentane can thus be cut down materially without any considerable sacrifice of accuracy.

In the standardization of lamps at the Bureau the pentane used is always kept below 0.635 in density. The values certified may therefore be considered as correct for a density of 0.630. No correction need be made for pentane below 0.635, but above that density correction is desirable. For example, if the pentane used runs up to 0.650, the candlepower obtained is presumably 2 per cent above that certified for the lamp, and this density is likely to be reached if a gallon of pentane is used without removing the residue from the saturator.

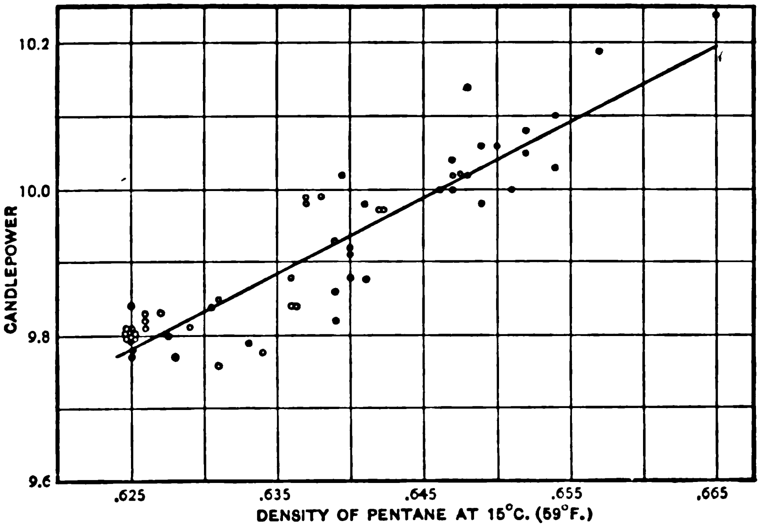

Fig. 2.—*Variation of candlepower of pentane lamps with density of pentane*

It should be noted that the above discussion refers to pentane which is initially fairly pure, as shown by the permanganate test. If the fresh pentane contains impurities, these are usually concentrated by the fractional distillation in the lamp, and the result may be an increase in candlepower greater than that given above.

V. EFFECTS OF ATMOSPHERIC CONDITIONS

It is usually assumed that the effect of all atmospheric conditions is the same on all flames and is therefore automatically corrected when flames are compared with flames, but it is sometimes necessary to know the amount of departure from the normal value, as when flame standards are compared with electric lamps. The dependence of flame intensity on the composition of the air is so complicated a matter that the determination of exact corrections for vitiation of the air is impracticable, and when observations are to be reduced to normal values good ventilation is indispensable so that no such corrections shall be needed. With pure air, however, there are considerable variations in candlepower because of variations in the amount of moisture and in the barometric pressure.

1. TEMPERATURE

Temperature might also be expected to affect the pentane lamp appreciably, but nearly all investigators have agreed that within the usual laboratory range it does not do so. In the work at the Bureau there has so far been available no means of changing temperature and humidity independently, and the effects of the two can not be separated with certainty. The results obtained can be represented about equally well by assuming that temperature has no effect or by making a small correction for temperature and using a correspondingly different factor for water vapor. In accordance with the usual custom the former practice will be followed, and the present discussion will be limited to the effects of barometric pressure and of water vapor.

2. BAROMETRIC PRESSURE

In general, flames give less light when the barometric pressure is low, but the effects on different sorts of lamps are markedly different. For the 10-candlepower pentane lamp a change of 0.6 per cent per centimeter (1.5 per cent per inch) was found at the

Physikalisch-Technische Reichsanstalt,[9] while the result obtained at the English National Physical Laboratory [10] is 0.8 per cent per centimeter (2 per cent per inch), and more recent work [11] in England has verified the latter value for pressures near the normal. Various determinations at the Bureau have not been consistent, chiefly because of the small range of pressure obtained. The results for the determinations which should have been most reliable have varied from 0.6 to 0.8 per cent, and consequently the English value, 0.8 per cent per cm. has been used.[12] The chart of deviations given in Fig. 3 is plotted on this basis.

3. WATER VAPOR

Water vapor in the air lowers the intensity of the flame; the effect has been found to be proportional to the amount of water present. This amount is expressed in liters (h) of water vapor per cubic meter of dry air; in other words, in parts of water vapor per 1000 parts of dry air. The pressure (e) of the water vapor is determined by means of a hygrometer (preferably of the ventilated type) using tables adapted to the particular type of hygrometer. If the barometric pressure is represented by b,

$$h = \frac{e}{b-e} \times 1000.$$

A normal value (n) for the amount of water vapor must be chosen more or less arbitrarily. Then, if I_n is the normal intensity of a given flame (that is, the intensity when there are n liters of water vapor per cubic meter of dry air), the intensity I at any particular time is given by the equation

$$I = I_n[1 + (n-h)a].$$

The normal proportion of water vapor has been fixed at 8 liters for the pentane lamp; the correction factor (a) has been several times determined, but the agreement between results in different laboratories is not close. These determinations were rather fully discussed in one of the earlier articles mentioned;[13] it is sufficient to recall here that the National Physical Laboratory[14] found a to be 0.0066, whereas the Reichsanstalt[14] obtained 0.0055, and the Bureau of Standards 0.0057. The more recent English tests[14] have given 0.00625.

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[9] J. f. Gas. u. Wasser., **49**, p. 561; 1906.

[10] Electrician (London), **53**, p. 751, 1904; J. Inst. of Elect. Eng., **38**, p. 271, 1906–7; J. Gas Light., **99**, p. 232, 1907; N. P. L., Collected Researches, **3**, p. 49, 1908.

[11] Butterfield, Haldane, and Trotter: J. Gas Light., **115**, p. 290, 1911; and Amer. Gas Light J., **95**, p. 145, 1911.

[12] In the Transactions of the Illuminating Engineering Society, **5**, p. 776, 1910, it was inadvertently stated that the factor 0.6 is used, when it should have been said that this factor was obtained from the data then reported on.

The method of testing lamps at the Bureau furnishes continual data for the redetermination of the correction factor, and complete calculations have been made using the results up to the beginning of the present year on all lamps whose tests have included a range of 5 liters of water vapor or more. To reduce the labor of calculation the values obtained each time a lamp is placed on the photometer have been grouped together. Some insignificant changes in the data published in 1910 have been made to correct for slight errors introduced by the barograph then used, and the revised results are given in Part I of the table below. These data include 628 groups of sets, or about 30 000 individual settings of the photometer. The data obtained from later tests are summarized in Part II of the table; they represent about 2300 groups of sets, or perhaps 75 000 individual photometer settings.

Water Vapor Correction Factors

I. OBSERVATIONS OF 1910

Lamp	Times on photometer	Weight	Factor a
Chance 116	74	174	0.00568
Chance 118	23	22	.00565
Sugg 171	62	130	.00565
American 25	16	11	.00584
American 74	19	48	.00564
American 157	11	8	.00581
American 162	7	9	.00572
Weighted mean value of a			.00567

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[13] Trans. Ill. Eng. Soc., **5**, p. 766; 1910.

[14] Loc. cit.

Water Vapor Correction Factors—Continued.

II. OBSERVATIONS OF 1911-12

Lamp	Times on photometer	Weight	Factor a
Chance 116	135	226	0.00586
Chance 118	177	339	.00552
25 other lamps	264	269	.00569
Weighted mean value of a			.00567

In assigning weights to individual lamps, allowance was made both for the number of times on the photometer and for the range of humidity covered. Since ranges as small as 5 liters were included, giving a total variation of only 3 per cent in these cases, and some of the lamps were on the photometer only six times, the results from individual lamps can not be expected to agree very closely. However, only two lamps gave a value for *a* below 0.0050, and the highest value obtained was 0.0066. The mean result checks the former one even more closely than could be expected, and there seems to be no room for doubt that, at least in the Bureau laboratory, the effect is very definitely and consistently represented by a factor of 0.57 per cent per liter of water vapor. This factor has been used in plotting the chart which is reproduced in Fig. 3.

4. CHART OF DEPARTURES FROM NORMAL VALUE

This chart has been so plotted that the departure of a lamp from the normal value can be read directly from it when the barometric pressure and the readings of the wet and dry bulb thermometers of a ventilated hygrometer are known. The hygrometer may be either a sling psychrometer such as is used by the United States Weather Bureau or a mechanically ventilated instrument like the Assmann psychrometer. If an ordinary stationary hygrometer is used, the covering of the wet bulb should be only one thickness of very thin material, and the reading should be taken at the lowest point to which it can be brought by vigorous fanning.

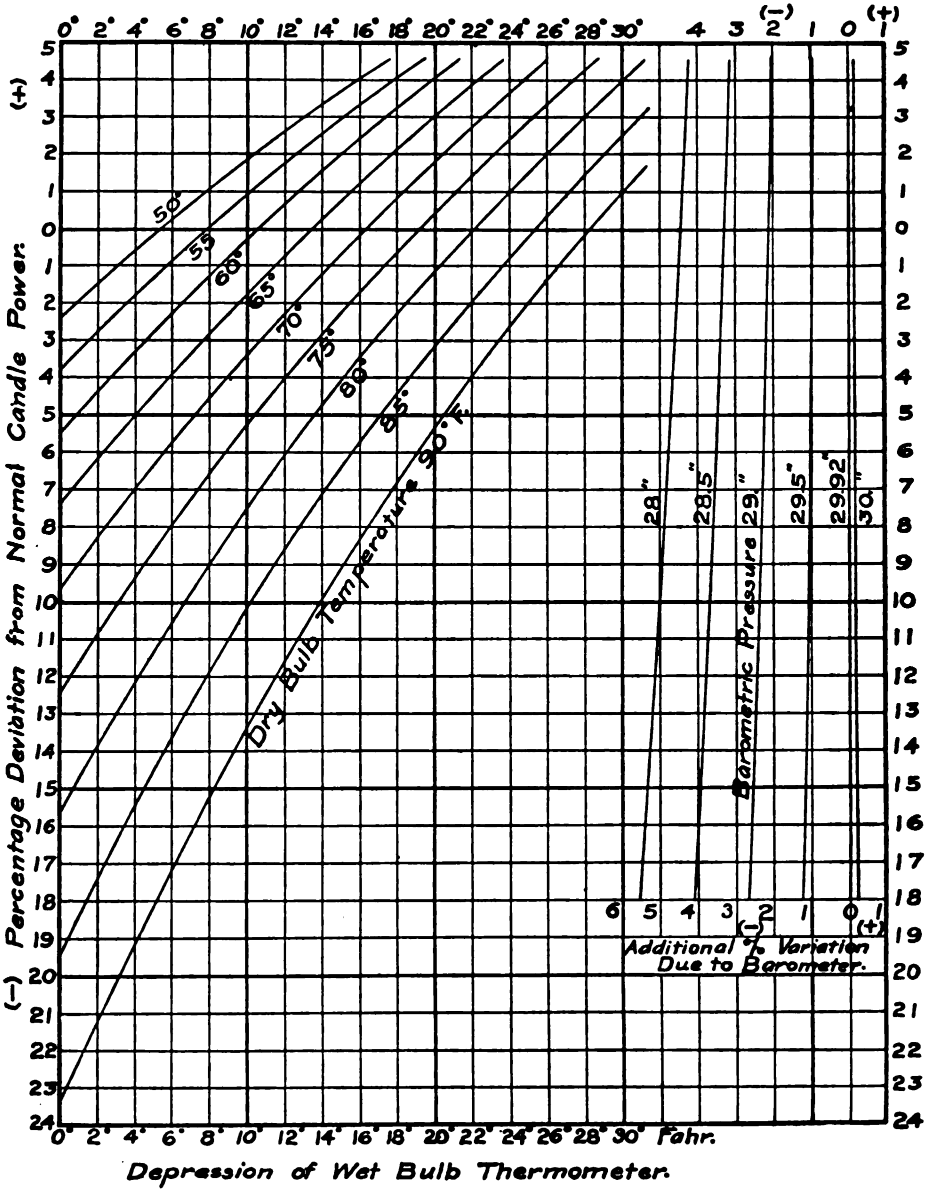

Fig. 3.—*Variations of candlepower of pentane lamps with humidity and barometric pressure*

The curves at the left of the chart give the percentage deviation from normal candlepower which corresponds to given temperature and wet-bulb depression when the barometric pressure is normal, which for the pentane lamp is 760 mm (29.92 inches). When the pressure is different from this the additional deviation can be found from the curves at the right, as follows: First read off the deviation in the regular way as if the barometer were normal, and note this; then from this point pass horizontally across the sheet to that curve at the right which represents the actual pressure. Vertically above or below the point at which this curve is reached will be found the amount to be added to the deviation as read from the first curves. This added amount is made up chiefly of the direct effect of pressure on the candlepower, but it includes also a proper allowance for the fact that the amount of water vapor which corresponds to a given pair of bulb readings depends somewhat on the barometric pressure.

The chart is plotted for the pentane lamp, but so far as we know it may be applied to other flames without introducing serious errors. It would certainly be justifiable to measure gas flames, for instance, with electric standards and to correct the observed candlepowers to obtain normal values according to the chart.

5. VARIATIONS OF HUMIDITY IN THE UNITED STATES

In order to give some idea of the amount of variation in water vapor which occurs from season to season data calculated from the records of the Weather Bureau which give the state of the outdoor air have been plotted in Fig. 4. In general the amount of moisture is small in winter and large in summer; the average for May and for October is practically the same as for the whole year. The variation from day to day is often great, especially in the spring and fall, but the monthly averages show considerable regularity from year to year. The curves are plotted from the averages of observations for five years.

The normal values of humidity adopted in Europe are lower than the average for nearly all parts of the United States; consequently, the average of uncorrected candlepowers of flame standards in this country runs somewhat lower than the normal intensities. The following table gives the average amounts of water vapor at several cities for the period of five years plotted in Fig. 4. The last column gives the corresponding departure of a pentane lamp from its normal value, which is practically the percentage of difference between the nominal and the actual average candlepower of any source which is measured by the lamp.

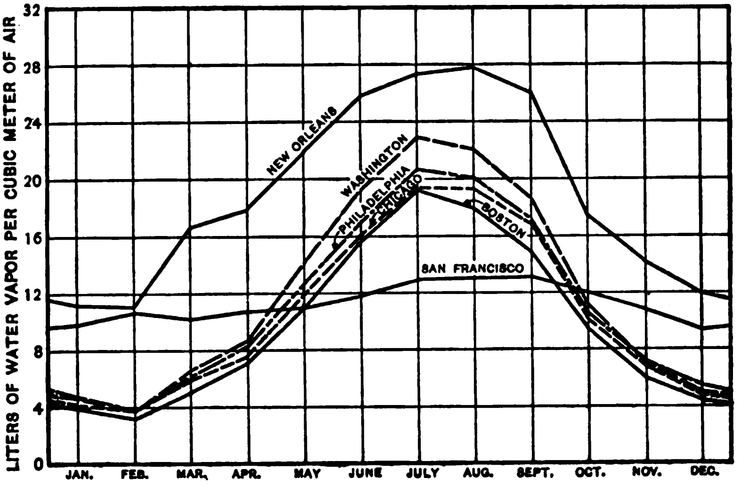

Fig. 4.—*Average water vapor content of the air at various cities, 1904–1908*

Average Water Vapor and Pentane Candlepower in the United States

Place	Average water vapor (liters per cubic meter)	Per cent departure of pentane lamp from normal value
Boston	9.9	1.1
Omaha	10.3	1.3
Chicago	10.6	1.5
Philadelphia	11.2	1.8
San Francisco	11.3	1.9
Washington	12.0	2.3
New Orleans	19.1	6.3

VI. SUMMARY

In this paper we have attempted to describe fully the method of testing pentane lamps at the Bureau of Standards, to give brief general directions for the use of the lamps, to discuss more fully the question of fuel, and to furnish data on the effects of pressure and moisture in a form which may be useful for those who have occasion to reduce observations on flames to normal candlepower values. Such new data as has been introduced has been obtained in the laboratories of the Bureau, and our acknowledgments are due to Dr. Rosa, under whose direction the work has been carried on, and to Mr. G. J. Schladt, who has assisted in most of the tests.

WASHINGTON, August 2, 1913.

TESTING POTENTIAL TRANSFORMERS

By H. B. Brooks

The ratio and phase angle of an instrument transformer may be accurately determined by laboratory methods. The commercial importance of such transformers has stimulated the development of accurate methods in recent years.[1] In many cases, however, it is not practicable to dismount transformers and send them to a laboratory, and a method is wanted which, while giving all needed accuracy, can be carried out at the point of installation, using commercial instruments and the ordinary supply voltage. Such a method of testing potential[2] transformers will now be described. No claim for originality of principle is made, as the only novel feature is the use of facilities which are available in any properly equipped a. c. power plant, in addition to a potential transformer whose ratio and phase angle are known.

Briefly, the idea of the method is as follows: From the practical point of view, an error in ratio or phase angle which produces a visible error in the reading of an indicating wattmeter is an error which needs to be known, while errors smaller than this are negligible. We may therefore use an indicating wattmeter in such a way that differences in ratio or phase angle of an unknown transformer and a standard transformer have the best possible opportunity to produce a deflection. By properly choosing conditions, this deflection may be readily made to give the numerical values of the quantities desired.

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[1] Rosa and Lloyd, This bulletin, **6,** p. 1; 1909; Reprint No. 116. Agnew and Fitch, Elec. World, **54,** p. 1042; 1909; Reprint No. 130. E. Orlich, Elektrotechnische Zs., **30,** pp. 435, 466; 1909. L. T. Robinson, Trans. Am. Inst. Elec. Eng., **28,** p. 1005; 1909. F. A. Laws, Elec. World, **55,** p. 223; 1910. Sharp and Crawford, Trans. Am. Inst. Elec. Eng., **29,** p. 1517; 1910. Agnew and Silsbee, Proc. Am. Inst. Elec. Eng., **31,** p. 1267; June 1912.

[2] There is some discussion as to whether the term "voltage transformer" should not be used to the exclusion of the term "potential transformer." At the present time, both expressions are in use.

The primary windings of the standard transformer and the transformer to be tested are connected to the same supply, as shown in Fig. 1. The secondary windings are connected in series so that their voltages are opposed. The secondary voltages will be nearly equal and will rise and fall in unison as the line voltage varies. The thing to be measured is the difference between the two secondary voltages, which difference in general would be only a few volts. As the lower end of the scale of an alternating-current voltmeter is practically useless, this small voltage can not be measured satisfactorily with even a low-range voltmeter. However, a 5-ampere indicating wattmeter may be used as a voltmeter by separately exciting its current coil.[3] This may be done by passing 5 amperes through the coil to a lamp load. This exciting current must not be drawn from either of the two transformers whose ratios are to be compared, but must come from the secondary of any other available transformer connected to the same phase as the transformers under comparison. The current through the series coil of the wattmeter should be kept at approximately 5 amperes, but this current

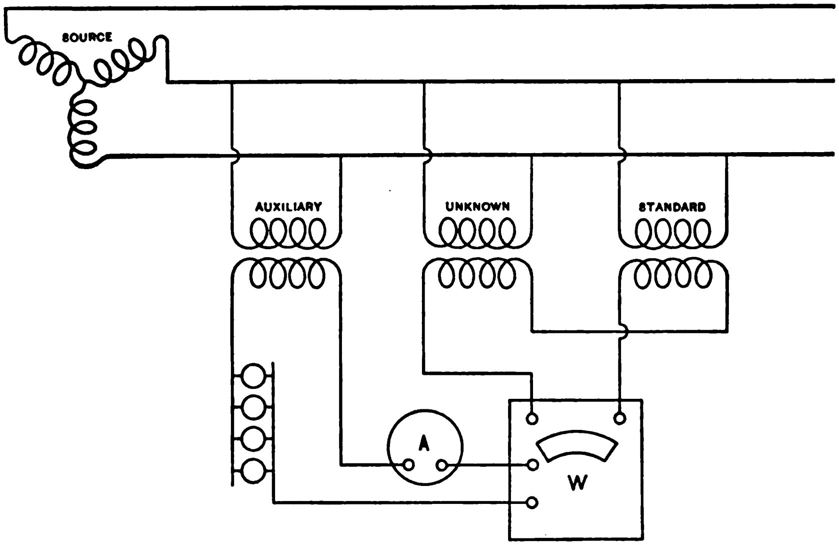

Fig. 1.—*Diagrammatic plan of connections for potential transformer testing*

needs to be measured with only moderate accuracy. The potential circuit of the wattmeter may now be used as a voltmeter to measure the small difference in the secondary voltages of the two transformers under comparison. For example, if the wattmeter is made for 5 amperes, 150 volts, 750 watts, and has a 150-division scale, then one division is 5 watts, and will be given by 5 amperes in the current coil and 1 volt on the potential circuit; hence the difference between the two secondary voltages, in volts, will be shown by the number of divisions deflection of the wattmeter. Since the ratio of good voltage transformers changes very little with ordinary fluctuations of line voltage, the difference of the secondary voltages will be practically constant; as the wattmeter reading is steady and can be taken to one-tenth of a division, the ratio of one transformer in terms of the other can be read to 1 in 1000. If the wattmeter has a 75-volt range, this may be used, and the reading will be doubled; that is, one volt difference between voltages will give two divisions deflection. It is obvious that with a wattmeter having a still lower voltage range, say 30 volts,[4] the difference between the secondary voltages could be still more accurately read.

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[3] A similar use of the wattmeter is described by Drysdale, Electrician, 57, p. 783; 1906.

The question as to which transformer has the greater ratio may be easily answered from the fact that increasing the noninductive load on the secondary always lowers the secondary voltage, and thus increases the ratio of transformation. If the reading of the wattmeter is up scale when there is no load on the secondary of the transformer under test, and if this reading increases as successive lamps are connected to the secondary of the transformer under test, this shows that at no load the voltage of this transformer is lower than that of the standard transformer. Similarly, if the deflection is below zero with no load, and the addition of load brings the deflection up through zero to a reading on the scale, this shows that at no load the voltage of the transformer under test is higher than that of the standard transformer. In this case the voltage leads to the wattmeter should be reversed at the start to bring the readings on the scale; they will decrease as load is gradually applied, and pass through zero, when the leads may be replaced in the original position.

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[4] With this range, at 60 cycles, no error due to mutual inductance enters, for two usual types of portable wattmeter. It is not advisable, in general, to reduce the range below 30 volts.

It is obvious that the above method is a suitable one for determining the regulation of power transformers, by using one transformer of a bank on no load as the standard transformer, and determining the drop of voltage of another transformer as the load on it is increased. This method is similar in principle to the one described by Drysdale,[5] but differs in important details. In his method the voltage circuit of the wattmeter is connected to the secondary of the standard transformer, and the current coil of the wattmeter, with some added resistance, is used as a low-range voltmeter to measure the difference of the secondary voltages. The method described in the present article inverts these uses of the two coils, the current coil being the one which is separately excited, and the voltage circuit being used as the low-range voltmeter. This has the advantage of drawing a very much smaller current from the transformers under comparison, and thus avoiding what might be an appreciable error in the case of small transformers.

If the preceding test for ratio is made with the primaries connected to one phase of a two-phase circuit, a determination of the difference of the phase angles of the two transformers may then be made by connecting the wattmeter series coil and 5-ampere lamp load to the other phase. Before doing this, the ratios of the transformers should be made equal by loading the secondary of one or the other with lamps or other noninductive load.[6] The current taken by this load should be determined; if it must be applied to the standard transformer in order to make the ratios equal, the value of phase angle of the standard transformer corresponding to the given load may be taken from a curve plotted from the certified values.[7] The small voltage shown by the wattmeter with its current coil on the second phase is a measure of the difference of the phase angles of the two transformers, with the given secondary loads. For example, suppose that the wattmeter constants are those previously referred to, and the 150-volt potential circuit is in use, so that one division deflection is given by 1 volt applied to the potential circuit. Suppose the deflection is 0.3 division when the 5-ampere current in the series coil is drawn from the second phase of the two-phase circuit while the primaries of the two voltage transformers are on the first phase. The 0.3 volt divided by the secondary voltage (say, 110) of the transformer under test equals 0.0027. This number is the sine of the small angle by which the phase angles of the two transformers differ. By reference to a table of natural sines,[8] the angle is found to be 9 minutes. Hence 0.1 division of the wattmeter corresponds to 3 minutes; by using the 75-volt range of the wattmeter, 0.1 division will correspond to 1.5 minutes.

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[5] Electrician, 65, p. 644; 1910.

[6] The writer is indebted to Dr. P. G. Agnew and Mr. F. B. Silsbee for this and other helpful suggestions.

[7] Such an interpolation is easily made, since the ratio and phase-angle curves of potential transformers are sensibly straight lines.

It remains to determine which of the two secondary voltages is leading the other. To test this point, use may be made of the fact that increasing a noninductive load connected to the secondary of a potential transformer tends to make the reversed secondary voltage lag behind the primary voltage. With the connections made for phase-angle test as just described, and the wattmeter reading 0.3 division up the scale, connect one or more incandescent lamps to the secondary terminals of the transformer under test, without disturbing any of the former connections. If the deflection of the wattmeter is increased, this shows that a reading up scale denotes that the secondary voltage of the transformer under test lags behind that of the standard transformer. If the application of the lamp load to the transformer under test sends the wattmeter reading down below 0.3 division, this shows that a reading up scale denotes that the secondary voltage of the transformer under test leads that of the standard transformer.

If a 2-phase circuit is not available, a 3-phase to 2-phase arrangement of transformers may be used. If this is not convenient, the test for phase angle may be made by exciting the wattmeter series coil from another phase of a 3-phase circuit. In this latter case, however, the wattmeter reading must be multiplied by 1.16 (the reciprocal of 0.866) in order to get the deflection which would be given if test were made on a 2-phase line. The calculation is then made as before. The phase-angle test may also be made with the series coil connected to the third phase as a check. If the deflections are slightly different from those obtained when phase 2 is used, the mean of the two values may be taken.

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[8] If a table of natural sines is not available, the angle (in minutes) may be obtained by multiplying the quotient of the two voltages by 3438; thus, 0.0027 times 3438 equals 9.+ This assumes that the sine of a small angle is equal to the angle expressed in radians. For the small phase angles of instrument transformers this assumption introduces no appreciable error.

Figure 1 shows no connected load on the secondary of the transformer whose ratio and phase angle are to be determined. However, any desired load may be connected to it and the comparison made in the same way. The load is simply connected to the secondary terminals without disturbing any of the other connections.

To test the accuracy of the foregoing method, two 5500 to 110 volt potential transformers were compared at three secondary loads. The test was then repeated, using an accurate laboratory method. The values for ratio by the two methods agreed to within 0.02, 0.05, and 0.08 per cent for the three loads, which were, respectively, light load, rated load, and twice rated load. The values of phase angle by the two methods agreed to within less than half a minute. The wattmeter used was provided with a 30-volt potential range especially for the test.

WASHINGTON, February 7, 1914.

COMPARISON OF THE SILVER AND IODINE VOLTAMETERS AND THE DETERMINATION OF THE VALUE OF THE FARADAY

By G. W. Vinal and S. J. Bates

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I. INTRODUCTION

Of the many electrochemical reactions which may theoretically be employed to determine the faraday, i. e., the quantity of electricity associated with a chemical equivalent in any electrochemical change, that of the deposition of silver from a solution of silver nitrate is the only one that has been extensively investigated. The values which have been accepted for the faraday from time to time have almost entirely been based upon results with the silver voltameter. This naturally resulted from the fact that the international ampere is defined in terms of the silver deposited under more or less rigorously fixed conditions, and hence this instrument has been the subject of many thorough investigations both by the national standardizing laboratories and by private individuals.

As a result of these investigations it has been possible for the past few years so to define the conditions to be used in connections with the silver voltameter that a reproducibility of 1 or 2 parts in 100 000 may be obtained. Until recently no other voltameter had attained anything approaching such a degree of precision

A little over a year ago, however, Washburn and Bates[1] published the results of a study of an iodine voltameter which they had devised and which was found to have a reproducibility of the same order as that of the silver voltameter. The apparently complete reversibility and purity of the electrochemical reaction in the iodine voltameter, coupled with the fact that no solid deposit is obtained, made it a particularly valuable reaction to employ for determining the faraday and warranted very exact electrical measurements. Since the Bureau of Standards had as a result of recent work on the silver voltameter exceptional facilities for such measurements, arrangements were made for the comparison during the summer of 1913 of the silver and the iodine voltameters at the Bureau of Standards.

II. ARRANGEMENTS FOR THE WORK

So far as the methods of making the silver deposits and washing, drying, and weighing them are concerned, no essential changes from those previously employed[2] at the Bureau of Standards were made. But the methods of measuring the current had to be somewhat modified owing to the high resistance of the iodine voltameters and the smaller current to be employed. An electromotive force of 240 volts was used to pass a current of one-fourth of an ampere through the circuit containing the voltameters and the ballast resistance of about 400 ohms. This necessitated particularly high insulation owing to the damp weather which is prevalent in Washington in summer. Fortunately this was obtainable by mounting the galvanometers and all apparatus on paraffin and using paraffin insulators to support all wires pertaining to the circuit. The circuit is shown diagrammatically in Fig. 1 The current was measured by means of a Wolff potentiometer (P), and also by directly balancing (B) the electromotive force of a Weston standard cell (No. 109) maintained at 28° in oil against the fall in potential across two 2-ohm resistance standards (R), through a second galvanometer, similarly to the method previously described.[1] To eliminate the errors of the potentiometer, however, the dials were set to the voltage of the cell as nearly as possible and balanced with the standard cell on the same terminals to which the emf of the standard resistance was applied. To facilitate this a double pole, double-throw switch (S_2) with all joints soldered and embedded in paraffin was used. Q is a series resistance for quick adjustment of the current, A is an ammeter for convenience, C the compensating resistance usually about 590 ohms, K is a Kelvin rheostat for fine regulation, S_1 is the main switch to throw the current on or off through the voltameters V. As a test of the circuit a comparison of the two methods of measuring the current was made when the humidity was 75 per cent and they agreed to within 2 parts in 1 000 000. All of the experiments were made under lower humidity conditions, and, when necessary, refrigerating coils were used to reduce the humidity of the room. A photograph, Fig. 2, shows the voltameters and some of the control apparatus.

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[1] J. Am. Chem. Soc. 34, pp. 1341, 1515; 1912.

[2] This Bulletin, 9, p. 151, Reprint No. 194.

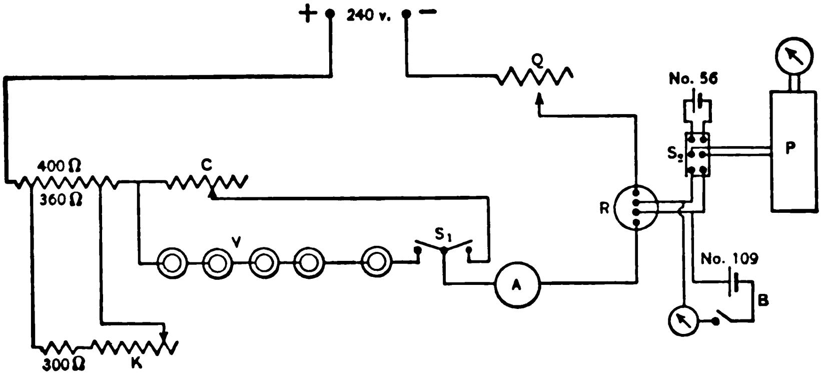

Fig. 1.—*The circuit*

As the potassium iodide solution in the iodine voltameters has a high temperature coefficient of conductivity and was subject to considerable heating by reason of its high resistance, some trouble was anticipated in maintaining the current at constant value, but this was avoided by immersing the iodine voltameters to a little above the V tube in large water baths. At the beginning of an experiment the drift in current due to heating in the voltameters was rapid for about five minutes, after which it decreased and finally became surprisingly steady during the greater part of the experiment.

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[1] This Bulletin, 9, p. 179, Reprint No. 194.

Some of the experiments were at 0.25 ampere for four hours; in all of these except the first two the current was maintained constant during the experiment. In the other experiments a current of 0.05 ampere was used for 20 hours but the current was not measured against the standard cell and resistance. For the purpose of computing the value of the faraday it is not necessary to measure the current by cell and resistance. It was, however, deemed advisable to do so in some cases at least so that the silver voltameter determinations might be connected with previous work at the Bureau of Standards. For this purpose the same standard cell and resistances were again employed as in the previous investigation. Comparisons of these with the standards maintained at the Bureau showed only very slight changes to have taken place.

III. THE VOLTAMETERS

A. THE IODINE VOLTAMETERS

1. APPARATUS AND MANIPULATION

The three iodine voltameters used were of the same type as those previously employed by Washburn and Bates. The apparatus, which is shown in Fig. 3, consists essentially of two upright limbs connected by a V tube. At the bottom of each limb is an electrode. The anodes consist of a platinum iridium alloy, it having been found that iodine is without appreciable effect on such an electrode, though one of pure platinum is attacked. Since the cathode solutions were not to be analyzed in the present investigation, it was permissible to use platinum electrodes for the cathodes. The electrodes were sealed into glass tubes, through which ran the electrical connections to the outside. These tubes as well as the capillary tubes through which the solutions were poured around the electrode come out through small openings in the caps at the top of the limbs. The joints between these tubes and the caps are made air-tight by means of short pieces of rubber tubing.

In order to prevent diffusion within the voltameter and also to prevent rapid changes in the resistance of the voltameters due to heating, the voltameters were placed in large water baths.

The voltameter is first filled through the side tubes with a 10 per cent solution of potassium iodide, which has been evacuated under an air pump to remove dissolved air. At the cathode side about 10 cc of a concentrated solution of potassium iodide (1 g salt to 1 g water) is then run down the capillary tube and this is immediately followed by about 20 cc of a concentrated solution of iodine and potassium iodide, which completely covers the electrode. In a similar manner the anode is surrounded by about 25 cc of the concentrated solution of potassium iodide.

At the conclusion of a run the solution in the cathode limb is discarded after having been sucked into a flask through the capillary and delivery tubes.

The amount of iodine formed at the anode by the passage of the current is determined by titration with a standard solution of arsenious acid. The theory of this titration and the calculation of the conditions which reduce the error to about 0.001 per cent have been previously discussed.[4] After the first rough weighing of one of the silver voltameters, the approximate quantity of electricity that has passed through the system, and hence the approximate amount of arsenious acid solution necessary for the titration, are calculated. An amount of the standard solution about one drop less than this is weighed out into a liter Erlenmeyer flask, and disodium phosphate solution added to control the hydrogen ion concentration. The flask is then fitted to the delivery tube so that the tip of the tube is below the level of the liquid and the anode solution quietly pulled up the capillary tube and over into the flask ("A," Fig. 2) by applying a gentle suction to the latter. The solution is then mixed and the titration completed in the manner described below.

2. CHEMICALS AND SOLUTIONS

The water employed for all of the solutions used in connection with the work of the iodine voltameter was obtained by redistilling the distilled water of the laboratory from alkaline permanganate, the first and last fractions of the distillate being discarded.

The potassium iodide was obtained by recrystallizing J. T. Baker's product until it was no longer alkaline to phenolphthalein. Because of the damp weather prevalent during this investigation, the potassium iodide was kept in desiccators over calcium chloride.

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[4] J. Am. Chem. Soc., **30**, p. 31; 1908; **34**, p. 1353; 1912.

The concentrated iodine solution which was used for surrounding the cathode was prepared by dissolving 910 g of C. P. iodine and 585 g of potassium iodide in 320 g of water. The dilute standard iodine solution was prepared by diluting the concentrated solution till it was about 0.01 normal. Its strength was determined by titrating it against the dilute standard arsenious acid solution.

The standard arsenious acid solution was prepared by dissolving 240 g of Kahlbaum's arsenious acid which had been recrystallized from conductivity water in a solution containing 120 g of J. T. Baker's C. P. sodium carbonate. The solution was then made up to approximately 5 liters and kept in a 5-liter glass bottle. The bottle was fitted with a delivery tube containing a stopcock and with a three-way tube through which hydrogen passed as the solution was withdrawn by means of the delivery tube. This three-way tube was attached to a manometer to indicate the pressure of hydrogen within the bottle and to Geissler bulbs which contained some of the same solution as was in the bottle and through which the hydrogen bubbled before entering the bottle.

It has been discovered in the previous investigation that the arsenious acid solution slowly oxidized. Hence, before beginning this investigation the solution was practically freed from dissolved air by slowly bubbling hydrogen through it. This was led in by means of the tube which afterwards served as the delivery tube, and which reached to the bottom of the bottle. After hydrogen has been bubbling through the solution for 24 hours, the stream of hydrogen was attached to the Geissler bulbs, care being taken that no air was permitted to enter the bottle. The pressure of hydrogen within the bottle was then raised to and maintained at a pressure equal to 4 or 5 cm of mercury greater than atmospheric pressure.

The hydrogen which was used for this purpose was prepared from C. P. zinc and sulphuric acid in a Kipp's generator. It was passed through a wash bottle containing alkaline permanganate and then over reduced copper contained in a quartz tube. This tube and the copper were kept red hot all the time during the course of this investigation by means of an electric heating device. From the quartz tube the hydrogen was led to the bottle containing the standard solution by means of a flexible copper tubing.

The bottle was kept in a large tank or pail of about 20 liters capacity. This pail was filled with water to prevent condensation of moisture on the upper part of the inside of the bottle due to temperature changes in the surroundings. The whole was mounted on a turntable in such a manner that the delivery tube might be swung directly over the mouth of a flask resting on the pan of a large Rueprecht balance.

The dilute arsenious acid solution was prepared by diluting about 10 g of the standard solution to 100 times its weight. This solution was not protected from the air and since it slowly oxidized, a fresh lot was prepared every week or 10 days. It was compared with the dilute iodine solution every three or four days; in this way it was possible to determine the strength of the solutions so that no error greater than 5 parts in 1 000 000 was introduced because of a change in their concentration.

3. METHODS OF STANDARDIZATION AND ANALYSIS

For the careful standardization of the arsenious acid solution, it was necessary to prepare a quantity of pure iodine. For this purpose potassium permanganate was added to an acid solution containing an excess of potassium iodide and the precipitated iodine after having been washed by decantation till the wash water was no longer acid, was dried in the centrifuge. It was then distilled from a retort and caught in a molten condition in a flask. The iodine was broken up in a dry mortar and kept in a desiccator over sulphuric acid, from there it was transferred as needed to the sublimation apparatus. This consisted of a Jena gerãthe glass tube, Fig. 4, about 100 cm long and 3 cm diameter. Into one end of it fitted a ground-glass stopper through which a current of air could be passed. This air was bubbled through a solution of alkaline permanganate, through two wash bottles containing sulphuric acid and then passed through a tube containing phosphorus pentoxide which had been recently sublimed into it. At the end nearest to the subliming apparatus this tube was closed by means of a stopcock, which was joined with Khotinski cement to the glass stopper of the subliming tube. During the course of the experiments very little moisture reached the phosphorus pentoxide and that only at the end farthest from the subliming apparatus.

The iodine in a porcelain boat is placed inside the sublimation apparatus at S just ahead of the glass stopper. Movable heating coils of manganin wire serve to sublime the iodine from this position down the length of the tube. The rate of sublimation could be conveniently controlled by regulating the temperature of the heating coils and the current of air passing through the tube. In passing from one end to the other of the sublimation apparatus the iodine was sublimed at least three times. It was then transferred without exposure to the atmosphere of the room, into a previously weighed quartz weighing bottle B, by means of the rake R which was operated through a narrow tube some 40 cm in length sealed onto the subliming tube.

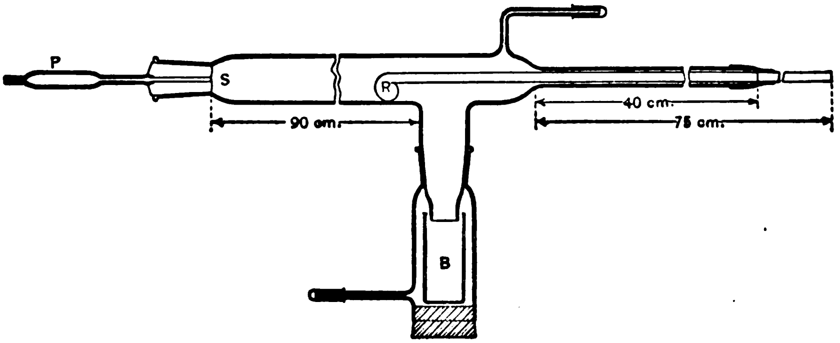

Fig. 4.—*Sublimation apparatus*

The iodine was weighed in the constant temperature room on the Oertling balance which has been previously described.[5] When empty the weighing bottles were always left on the balance pan at least four hours before a weighing was attempted, when they contained iodine they were left over night. The weighings were made by substitution, an empty weighing bottle serving as part of the counterpoise. The set of weights employed had been compared with the standard weights of the Bureau. It is believed that the weight of iodine was known to 0.02–0.03 mg.

For the first week or two of the present investigation the iodine voltameters did not check well and the arsenious acid solution could not be accurately standardized. It was found that the trouble lay in the method of weighing the solution. Up to June 26 the method was that employed in the previous investigation at the University of Illinois. Liter Erlenmeyer flasks were balanced on the two pans of a large Rueprecht balance, the desired amount of solution run into the flask on the left-hand pan, a rubber stopper which had been weighed with the flask inserted into its mouth and the weight of the added solution accurately determined. The previous work had been done during the spring of the year in a basement room which was not heated artificially. The room was quite cool and the variation in the amount of evaporation of the solution during the time required to draw off the solution and stopper the flask was not rapid enough to introduce an error greater than 0.002 per cent. The temperature of the room in which the weighings for the present investigation were made was between 29° and 31° C. This caused an uncertainty in the weighing which depended upon the length of time it took to transfer the proper amount of solution to the flask and to stopper it. This time was somewhat variable, since toward the end of the addition of the solution to the flask it had to be added slowly in order to get the weight within 0.1 g of that required for the titration, before the final weighing to a few tenths of a milligram was attempted.

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[5] This Bulletin, 9, p. 174, Reprint No. 194.

This uncertainty in the weight of the standard solution was greatly reduced by the following modification in the method of weighing. About 25 cc of water was added to both of the flasks on the balance pan, they were then balanced and it was determined whether or not the rate of evaporation of water from both of them was the same. The mouth of the counterpoise flask was somewhat larger than that of the flasks in which the solution was weighed, so it lost weight more rapidly. However, by adjusting the size of the opening by means of a small piece of paper, the rate of evaporation from the two flasks could be practically equalized.

The required amount of solution was then added, both flasks left unstoppered, and the weight determined as soon as possible. The rate of evaporation was again investigated, and if it were not the same as it was before the solution was added, an allowance was made for this. The uncertainty in the weight of solution taken was seldom over 0.5 mg, but is probably the greatest source of error connected with the iodine voltameters in this investigation. With practice this error was reduced, since toward the end of this investigation both the voltameters and the standardizations checked to 1 or 2 parts in 100 000.

After the arsenious acid solution was weighed out, the required amount of disodium phosphate solution was added to the flask. In the case of the standardizations some 30 g of potassium iodide was also added, and then the quartz weighing bottle was introduced into the flask and opened below the level of the liquid to prevent any loss of iodine vapor. When the iodine had completely dissolved, water was added till the volume of the solution was 250 to 275 cc.

The dilute arsenious acid solution was then run from a burette into the flask till the iodine color all but disappeared and the solution set aside for three to five minutes for equilibrium conditions to be attained. For the completion of the titration the flask containing the solution and another containing the same volume of water were set side by side on a large sheet of unglazed white paper before a north window. The arsenious acid solution was then added drop by drop till the iodine color just disappeared. It was possible by proceeding in this way and by comparing the appearances of the liquids in the two flasks to detect the effect of a single drop of the arsenious acid solution upon the iodine color. After determining the end point, about 1 cc of the dilute iodine solution was run in and the end point again determined. In this way three or more observations were always obtained for each end point; with practice and with favorable illumination it was possible to decrease the uncertainty in the end point to 0.02–0.03 cc of the dilute arsenious acid solution. This corresponds to an uncertainty in the titration of 5 or 6 parts per 1 000 000.

In order to get the iodine formed at the anode of the voltameter into a flask to be analyzed, a rubber stopper carrying the delivery tube was fitted to the flask containing the arsenious acid solution and the phosphate solution, in such a way that the end of the delivery tube dipped below the surface of the liquid. (Fig. 2.) The flask was then supported beside the voltameter and the delivery tube connected to the bulb at the top of the capillary tube by means of the ground glass joint. On applying a gentle suction to the flask the anode portion was sucked over, the last visible trace of iodine from around the electrode disappearing up the capillary by the time half of the solution contained in the anode limb had been sucked over into the flask. As a precaution, however, the entire anode solution was used to wash out the capillary and delivery tubes. The solution was then thoroughly mixed and the titration completed as described above.

4. STRENGTH OF THE STANDARD ARSENIOUS ACID SOLUTION

The data obtained for the standardization of the arsenious acid solution are given in Table 1. This table is divided into two parts, corresponding to the two methods of weighing the solution. The first column gives the date of the standardization, the second the number of grams of iodine taken (corrected to vacuo by adding 0.0099 per cent of the apparent weight). In the third is found the number of grams of arsenious acid solution used in the titration; the fourth gives the grams of iodine corresponding to 1 gram of the standard solution; this value will hereafter be referred to as the factor. The value for the factor, as calculated in the manner described below, is given in the next column, and in the sixth is found the difference in per cent between the value of the factor as found and as calculated.

The results show that even with the precautions taken the standard solution was oxidizing. In order to compare the standardizations and to determine the strength of the solution at any time the values of the factor found in column 4 were plotted against the corresponding days upon which the titrations were performed. It was found that for the period during which the second and more accurate method of weighing was employed a straight line could be drawn through the points in a satisfactory manner. From this line the strength of the solution for any particular day may be read off or the factor may be calculated from the equation of the line. The value for the factor F on the t^{th} day after June 30 is given by $F = 0.1081352 - 0.00000096t$, and therefore changes at a rate less than 0.001 per cent per day. The values for the factor given in the fifth column of Table 1 were calculated by means of this equation.

TABLE 1

Standardization of Arsenious Acid Solution

FIRST PERIOD

Date	Iodine	Arsenious acid solution	Factor found	Factor calculated	Difference in per cent
1913.					
June 4	4.81605	44.5100	0.108201	0.108193	+ 0.008
June 7	5.11905	47.3058	212	190	+ 0.020
June 11	4.97658	46.0003	186	186	0.000
June 14	2.89043	26.7085	221	183	+(0.035)
June 16	5.96126	55.1136	163	180	− 0.016
June 19	4.13730	38.2395	220	178	+(0.039)
June 21	4.78222	44.2131	163	176	− 0.012
Average deviation					0.011

SECOND PERIOD

Date	Iodine	Arsenious acid solution	Factor found	Factor calculated	Difference in per cent
1913.					
June 30	5.80150	53.6502	0.1081356	0.1081352	+ 0.0004
July 1	5.73071	52.9967	334	343	− 0.0008
July 3	5.39535	49.8957	326	323	+ 0.0003
July 9	4.50081	41.6258	254	266	− 0.0011
July 10	5.41817	50.1110	233	256	− 0.0021
July 12	4.64987	43.0048	244	237	+ 0.0006
July 16	5.37630	49.7256	197	199	− 0.0002
July 17	5.98294	55.3427	071	189	−(0.0109)
July 19	5.78941	53.5518	086	170	−(0.0077)
July 21	4.93161	45.6139	163	151	+ 0.0011
July 22	5.00639	46.3064	144	141	+ 0.0003
July 23	5.31224	49.1342	169	132	+ 0.0033
July 25	5.15089	47.6395	222	112	+(0.0101)
July 28	4.91674	45.4787	108	083	+ 0.0023
July 29	4.70907	43.5590	078	074	+ 0.0004
July 30	5.77480	53.4188	042	064	− 0.0020
July 31	4.31213	39.8883	051	054	− 0.0003
August 1	5.18195	47.9361	012	045	− 0.0030
August 2	5.55903	51.4236	027	036	− 0.0008
Average deviation					0.0012

Of the standardizations obtained by the second method of weighing, those of July 17, 19, and 25 were not considered in placing the line, because they deviated widely from the other observations. That of July 17 is furthest from the calculated value, the difference being 0.011 per cent.

The average deviation of 0.0012 per cent is about what would be expected from the uncertainties in weighing the iodine, in weighing the solution, and in determining the end point.

For the first period, during which the method of weighing was unsatisfactory, it is extremely difficult to draw a line in a manner similar to that drawn for the second period. The slope of such a line, however, should be the same as that for the second period, since the change in the method of weighing could not have influenced the rate of oxidation of the solution. Having thus obtained the slope of the line, its position was chosen so that the positive and negative deviations were equal. The value for the factor for this first period was determined graphically.

B. THE SILVER VOLTAMETER

1. FORMS USED

Two forms of silver voltameter were used in all experiments, Smith's new form and the porous cup form. Both of these have been described in detail elsewhere.[6] They are shown photographically in Fig. 2. In the tables that follow in the next section it will be seen that the results of the absolute runs made with these voltameters are in good agreement with the best previous work. As in the case of the third series of experiments published by Rosa, Vinal, and McDaniel,[6] where the mean value of the Weston normal cell is given in terms of both forms of voltameters, so here we have included in the mean both forms of voltameters to obtain the value of the silver with which to compare the mean iodine deposits.

2. MATERIALS, ETC.

The details of the manipulation of the voltameters and the preparation of materials have all been described before.[7] The electrolyte was prepared from double-distilled water and silver nitrate especiallly prepared and tested for acidity by iodeosine and for reducing agents by potassium permanganate as described by Rosa, Vinal, and McDaniel.[8] The anode and cathode acidities of each voltameter were measured at the conclusion of the experiment. The mean acidity of the electrolyte at the beginning of the experiment and the cathode acidity at the end of the experiment were thus determined for each voltameter and corrections to the deposit could be made for the acid present according to the equation $Y = 4.5X$ where Y is the amount to be added to the deposit in parts per million and X the acidity of the electrolyte in parts per million. This correction was determined by Rosa, Vinal, and McDaniel and is described by them. In the present case the electrolyte was always very nearly neutral so that the corrections are very small in all cases.

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[6] This bulletin, 10, reprint No. 220. (In press.)

[7] Ibid., 9, p. 151, reprint No. 194.

[8] Ibid., p. 524, reprint No. 201.

IV. TABLES OF RESULTS

The details of each experiment made or attempted are given in Table 2. The experiment of June 6 which is designated as No. 1 we have omitted from the summary of results contained in Table 3 since during the run iodine from the cathode was seen to have migrated up this limb and over into the anode side, coloring the liquid in the connecting V-tube quite distinctly.[9] Before starting the experiment it had been suggested that the first run would be largely of a preliminary nature. Aside from this run the only silver voltameter measurements omitted in computing the results are those enclosed in brackets. One of them on July 22 deviates from the mean by about four times the average deviation of the others and hence may be called a gross error. Two others, on July 30, were found to be alkaline at the close of the experiment which is sufficient reason to discard them as shown in previous investigations.[10] Owing to a miscalculation which resulted in much too little arsenious acid solution being weighed out for two of the voltameters of run No. 9, but one accurate analysis of the iodine formed in this experiment was obtained.

In the column of remarks the experiments designated as "absolute" are those in which the current was maintained constant during the entire time of the run and measured in terms of a standard cell and resistance. In the "comparative" experiments this was not done.

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[9] This movement was prevented in subsequent runs by the addition of the few cubic centimeters of concentrated potassium iodide solution which was run into this limb just before the iodine solution. With this procedure, it was never possible to detect any coloration due to iodine more than one-third way up the cathode limb.

[10] Report of Int. Tech. Com., p. 157.

TABLE 2

General Table of Results

[LNF means large new form or Smith form; LPP means large porous pot form; SPP means small porous pot form.]

Date of run	No. of run	Silver voltameters						Iodine voltameters					Remarks
		Form	Acidity		Deposit corrected for acidity	Mean value	Average deviation	Date of titration	Factor	Deposit	Mean value	Average deviation	
			Mean	Correction									
			Pts. in 10^5	Mg	Mg	Mg	Pts. in 10^5			Mg	Mg	Pts. in 10^5	
1913 June 6	1	LNF	0.8	0.01	4079.20	4079.19	3_9	1913 June 7	0.108190	4799.35	4799.58	4_9	Trial experiment, ½ ampere, 4 hours. Discarded experiment because mixing occurred in the iodine voltameters. Current not maintained constant.
		LNF	.8	.01	4079.51					4799.82			
		LPP	.7	.01	4079.16								
		SPP	.9	.01	[4078.68]								
		SPP	.9	.01	4078.90								
13	2	LNF	.4	.01	4105.98	4105.82	5_4	14	0.108183	4828.76	4829.59	11_6	Comparative experiment, ½ ampere, 4 hours.
		LNF	.6	.01	4106.10					4830.24			
		SPP	1.2	.02	4105.52					4829.77			
		SPP	1.7	.03	4105.69								
18	3	LNF	.2	.00	4104.70	4104.69	1_8	20	0.108177	4828.38	4828.62	5_0	Absolute experiment, current steady, ½ ampere, 4 hours.
		LPP	.7	.01	4104.79					4828.86			
		SPP	.3	.00	4104.65								
		SPP	.1	.00	4104.61								
26	4	LNF	.6	.01	4099.10	4099.03	2_7	28	0.1081371	4822.22	4822.24	2_6	Do.
		LPP	1.2	.02	4099.17					4822.42			
		SPP	.9	.01	4098.89					4822.08			
		SPP	1.8	.03	4098.93								
July 1	5	LNF	1.1	.02	4397.16	4397.11	1_4	July 3	0.1081323	5172.58	5172.73	2_8	Comparative experiment, $\frac{1}{10}$ ampere, 20 hours.
		LPP	1.0	.02	4396.99					5172.87			
		SPP	1.3	.02	4397.15					[5169.85]			
		SPP	2.2	.04	4397.16								
9	6	LNF	.9	.01	4105.32	4105.23	2_2	11	0.1081247	4828.54	4828.51	2_9	Absolute experiment, current steady, ½ ampere, 4 hours.
		LPP	1.1	.02	4105.33					4828.69			
		SPP	1.3	.02	4105.20					4828.30			
		SPP	1.7	.03	4105.08								

TABLE 2—Continued

General Table of Results—Continued

Date of run	No. of run	Silver voltameters						Iodine voltameters					Remarks
		Form	Acidity		Deposit corrected for acidity	Mean value	Average deviation	Date of titration	Factor	Deposit	Mean value	Average deviation	
			Mean	Correction									
			Pts. in 10^6	Mg	Mg	Mg	Pts. in 10^6			Mg	Mg	Pts. in 10^6	
1913 July 14	7	LNP	2.0	.04	4122.86	4123.10	2_9	1913 July 16	0.1081199	4849.35	4849.42	3_6	Comparative experiment, $\frac{1}{10}$ ampere, 20 hours.
		LPP	2.5	.04	4123.29					4849.67			
		SPP	3.5	.06	4123.15					4849.24			
		SPP	5.0	.09	4123.08								
18	8	LNP	1.9	.03	4104.78	4104.75	4_3	19	0.1081170	4828.63	4828.60	0_9	Absolute experiment, current steady, $\frac{1}{2}$ ampere, 4 hours.
		LPP	2.0	.04	4105.09					4828.53			
		SPP	3.7	.06	4104.60					4828.63			
		SPP	4.0	.07	4104.54								
22	9	LNP	....	....	4184.27	4184.24	2_8	24	0.1081122	[4920.91]	4921.30	....	Comparative experiment, $\frac{1}{10}$ ampere, 20 hours. Omit LPP determination.
		LPP	3.5	.06	[4184.94]					[4920.99]			
		SPP	1.2	.02	4184.35					4921.30			
		SPP	1.2	.02	4184.10								
25	10	LNP	.1	.00	4100.27	4100.27	2_4	26	0.1081102	4822.36	4822.47	1_4	Absolute experiment, current somewhat unsteady. $\frac{1}{2}$ ampere, 4 hours.
		LPP	.3	.00	4100.20					4822.48			
		SPP	.0	.00	4100.14					4822.57			
		SPP	.1	.00	4100.47								
30	11	LNP	Alk.	....	[4105.35]	4105.16	0_8	31	0.1081054	4828.55	4828.44	1_7	Absolute experiment, current became unsteady during an electrical storm of unusual violence, $\frac{1}{2}$ ampere, 4 hours. Two large cups, alkaline; omit these.
		LPP	Alk.	....	[4105.24]					4828.36			
		SPP	.5	.01	4105.17					4828.40			
		SPP	.1	.02	4105.15								

In Table 3 are contained the summarized results and the computed values for the ratio of silver to iodine, the electrochemical equivalent of iodine, and the value of the faraday. Column 1 gives the number of the experiment corresponding to the numbers given in Table 2. Columns 2 and 3 contain the mean deposits of silver and iodine for each experiment. Under "calculated coulombs" we give the number of coulombs as calculated from the silver voltameter deposits, using the value 1.11800 mg per coulomb as defined by the London conference. These are therefore in international units. We also give the coulombs as calculated from the measurement of current and time when the absolute runs were made. These also are international unit coulombs, since they have been computed on the basis of the Weston normal cell taken as 1.0183 volts at 20° C and the international ohm. The differences between these are given in the next column. On the average the coulombs calculated from the voltameter are $\frac{1.5}{100\ 000}$ smaller than from the measurements of current and time. This is as it should be, since the voltameter measurements at the Bureau of Standards recently have given a value for the cell about 2 or 3 parts in 100 000 lower than the adopted value 1.0183. The slight ambiguity that arises in the term "international coulombs," due to the possibility of measuring them in terms of the silver voltameter and time, or in terms of the international ohm, volt, and time, is fully explained in Part IV of the series of papers by Rosa, Vinal, and McDaniel.[11] For the present purposes this difference is immaterial, because in computing the value of the faraday the international atomic weight for iodine is involved, which is expressed to only five significant figures.

The system used in weighting the several experiments was purely mathematical, based upon the fact that for each result the error is due to the combination of experimental errors entering from the value of the factor for the arsenious acid (z_1), from the titration of the iodine deposits (z_2), and finally from the determination of the silver (z_3). The final result Z is then a function of these three quantities, $Z = f(z_1 z_2 z_3)$.

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[11] This Bulletin, 10, Reprint No. 220. (In press.)

We may easily compute the probable errors of each of these factors from the average deviation. If we designate them as $r_1\ r_2\ r_3$ the probable error of the result of the experiment is given by

$$R^2 = \left(\frac{\delta Z}{\delta z_1}\right)^2 r_1^2 + \left(\frac{\delta Z}{\delta z_2}\right)^2 r_2^2 + \left(\frac{\delta Z}{\delta z_3}\right)^2 r_3^2$$

TABLE 3

Summary of Results

No. of run	Mean silver deposit	Mean iodine deposit	Calculated coulombs			Weight	Ratio silver: iodine	Electro-chemical equivalent of iodine	Value of the faraday (I=126.92)	Remarks
			From Ag. voltameter	From Cell and Res.	Diff.					
	mg	mg			pts. in 10^6					
2	4105.82	4829.59	3672.47			1.3	0.85013_8	1.31508	96 511	4-hour run
3	4104.69	4828.62	3671.45	3671.53	-2_2	3.0	07_5	518	504	Do.
4	4099.03	4822.24	3666.39	3666.55	-4_4	25.0	02_6	526	498	Do.
5	4397.11	5172.73	3933.01			22.2	05_6	521	502	20-hour run
6	4105.23	4828.51	3671.94	3671.84	$+2_7$	24.4	20_5	498	518	4-hour run
7	4123.10	4849.42	3687.92			16.2	22_6	495	521	20-hour run
8	4104.75	4828.60	3671.51	3671.61	-2_7	20.0	09_1	515	506	4-hour run
9	4184.24	4921.30	3742.61			20.8	23_0	494	521	20-hour run
10	4100.27	4822.47	3667.50	3667.65	-4_1	45.5	24_3	492	523	4-hour run
11	4105.16	4828.44	3671.88	3671.82	$+1_6$	100.0	20_4	498	519	Do.
	Arithmetical mean (No. 4—11)						0.85016	1.31505	96 514	
	Weighted mean (all observations)						0.85017	1.81502	96 515	

These calculations have been carried out and weights computed inversely as the square of the probable error. Some system of weighting seemed to be necessary since the later experiments were deemed more reliable than the earlier ones. The experiments numbered 2 and 3 have very small weights, owing to the difficulties in weighing out the arsenious acid at this time, so that they may practically be disregarded. We give the arithmetical mean of experiments 4 to 11 for comparison with the weighted mean. The differences are very small.

V. DISCUSSION OF RESULTS

A. THE SILVER-IODINE RATIO

In Table 3 the results of this investigation have been presented in three ways—(1) as the ratio of silver to iodine, (2) as the electrochemical equivalent of iodine, and (3) as the value of the faraday calculated from the iodine voltameter. The ratio has been given chiefly because it possesses certain advantages for discussing the results. If the increase in weight of the platinum bowls used as cathodes represented only the weight of silver electrolytically changed from the simple Ag + ions to metallic silver, and if the only reaction taking place at the anode of the iodine voltameter is the formation of iodine from iodide ions under the action of the current, then according to Faraday's law the amounts of silver and of iodine so found are in the ratio of the atomic weights of the elements.

Baxter,[12] who has made a very careful study of the atomic weights of silver and of iodine, as the result of early work gave 0.849997 as the value of this ratio. As a result of further work he arrived at the result 0.849930,[13] and more recently from a series of very concordant experiments he found the value 0.849906.[14] That calculated from the international atomic weights (1914) for silver and iodine, which are largely founded on Baxter's results, is 0.84998. The only other investigation of recent years which is comparable with the results of Baxter is that of Köthner and Amer,[15] who determined the silver-iodide silver-chloride ratio in eight closely agreeing analyses. Their result, on the basis of chlorine 35.457, gives 0.850013 as the value of the silver-iodine ratio.

It is not our purpose to discuss these atomic weight determinations. It is evident that our determination of the silver-iodine ratio is from 0.015 to 0.030 per cent higher than that calculated from purely chemical methods. It seems unlikely that further work employing the same chemical reactions as have been hitherto used would cause this discrepancy to disappear, although Baxter considers that further evidence upon the silver-iodine ratio is desirable.

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[12] Carnegie Public. No. 135, p. 101.

[13] Ibid., p. 108.

[14] J. Am. Chem. Soc., **32**, p. 1591 (1910).

[15] Ann. d. Phys., **337**, pp. 123, 362 (1904).

Our consistently higher results are in the direction of too heavy a deposit of silver or the formation of an insufficient amount of iodine. It may readily be suggested that the difference may be in part accounted for by inclusions of liquid in the silver deposit, but the conflicting results of previous observers do not permit us to estimate the amount. The last work by Laird and Hulett[16] indicates that deposits from pure solution probably do not contain more than 0.005 per cent inclusions. The whole question of inclusions is critically discussed by Rosa, Vinal, and McDaniel.[17] Their opinion is that the deposits so perfectly crystalline as formed from the purest $AgNO_3$ obtainable do not contain significant inclusions. It is hoped that the work being carried out on this important subject in several laboratories will definitely settle the matter shortly.

In connection with the iodine voltameter three possible sources of error suggest themselves.

1. The main reaction which takes place at the anode, resulting in the formation of iodine from iodide ions, may have been accompanied by another electrochemical reaction, such as the formation of oxygen which then remained dissolved in the solution.

2. Sufficient iodine may have been formed, but a slight amount of it reacted with the water or with the metal of the electrodes.

3. The iodine used to standardize the arsenious acid solution may not have been suffciently pure.

In the first place there is no certain difference between the results obtained using the current strengths of 0.05 ampere and of 0.25 ampere. The arithmetical means differ by 0.002 per cent while the weighted means differ in the opposite direction by 0.003 per cent. This shows that there is no appreciable error arising from such a reaction as the electrolytic formation of oxygen, for such a reaction would evidently be much greater with the higher current densities.

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[16] Trans. Am. Electrochem. Soc., **22**, p. 345; 1912.

[17] This Bulletin, **10**, 1913, Reprint No. 220. (In press.)

Secondly, had any of the iodine been lost by reacting with the platinum-iridium electrodes this fact would have been immediately noticed, for it was found in the previous investigation that the presence of the slightest trace of platinum—less even than that corresponding to a loss of 0.001 per cent iodine—so affected the color of the solution that the end point in the titration was quite uncertain.

In solutions of iodine which contain in addition potassium iodide, as did all of our solutions, the iodine exists almost entirely as the triiodide ion, I_3^-. Iodine may react with water in two ways; these may be most conveniently expressed in the ionic forms,

$$OH^- + I_3^- = HIO + 2I^-$$

and

$$6OH^- + 3I_3^- = IO_3^- + 8I^- + 3H_2O.$$

The equilibrium constants of these two reversible reactions have been calculated.[18] In accordance with these calculations the conditions of the titrations in the present investigation were so regulated, by controlling the hydroxyl ion concentration, that when equilibrium was attained, no appreciable amount of hypoiodite or of iodate were present. The calculations showed that even with a rather large variation of the hydroxyl ion concentration an amount of iodine less than 0.001 per cent would be lost. This was confirmed experimentally by adding different amounts of sodium phosphate to some of the solutions which were being analyzed. In this way the hydroxyl ion concentration was varied about fiftyfold. Such a change had no noticeable effect on the end point, that is, it affected the analytical results by less than 0.001 per cent.

The best evidence that the combined effect of errors due to the formation of electrolytic oxygen and to the loss of iodine through side reactions is negligible was obtained in the previous investigation on the iodine voltameter.

The reaction which takes place at the cathode of the voltameters is the formation of iodide ions from iodine, being just the reverse of that occurring at the anode. Hence, in order to determine the silver-iodine ratio or to calculate the Faraday it is just as feasible theoretically to employ the amount of iodine used up at the cathode as it is to employ the amount formed at the anode. In the previous investigation both of these amounts of iodine were determined, and it was found that they agreed with one another within the experimental error of 0.003 per cent. That is, within this limit no side reactions resulting in the formation of too little iodine at the anode occur; the reaction taking place at the electrodes is strictly reversible. The amount of iodine used up at the cathode was not determined in the present investigation because the analysis of the cathode solution is much more difficult experimentally than is that of the solution at the anode.

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[18] Washburn: J. Am. Chem. Soc., **30**, p. 31; 1908.

Thirdly, if any of this discrepancy between the silver-iodine ratios is to be ascribed to impurity in the iodine, this impurity would have had to consist of some oxidizing substance having a smaller equivalent weight than has iodine. The presence of an inert substance such as moisture would have caused a deviation in a direction opposite to that actually found. Special precautions were taken to eliminate from the iodine any oxidizing substance, such as bromine. As described above, the iodine was precipitated by means of potassium permanganate from a solution containing an excess of potassium iodide. The partly dried iodine was then distilled from a retort and caught in a molten condition, and finally it was repeatedly sublimed in a current of dry air. Any one of these three procedures should have practically eliminated any trace of chlorine or bromine which might have been present. The last step, the fractional sublimation, was carried out separately each time the arsenious acid solution was standardized. The procedure was not always the same; occasionally but three sublimations were employed, but more often five or six. It is scarcely possible that under such circumstances an amount of volatile impurity sufficient to account for an appreciable part of the discrepancy of (0.015 to 0.03 per cent) should have remained so constant in amount that the average deviations of the standardizations (see Table 1) were but 0.0012 per cent, an amount easily accounted for by experimental error.

Taking these various sources of error into consideration, it is probable that the amount of iodine calculated to have been found at the anode is within 0.005 per cent of that corresponding to the electrochemical change of iodide ions to iodine. The calculations of the value of the Faraday from this involves the atomic weight of iodine and the electrical measurements of the present investigation. It seems unlikely that the mean value for the Faraday (96 514 international coulombs) given in Table 3 is in error by more than 0.015 per cent.

The possibility of electrical leakage on the voltameter stands being a source of error was also considered, but tests easily made showed the insulation to be amply sufficient.

B. THE FARADAY

If the increase in weight of the platinum bowls of the silver voltameter be assumed to represent only the metallic silver formed from silver ions, then taking the atomic weight of silver as 107.88, the Faraday is defined as $\frac{107.88}{.00111800} = 96\,494$ international coulombs. From the iodine voltameter we obtained the value 96 514; the mean, 96 504, probably represents within 0.01 per cent the true value in international units.

Values in absolute units.—For theoretical purposes it is desirable that the value of the Faraday should be known in absolute units. We do not, however, think it advisable to emphasize this value at the present time, for the following reasons:

1. Electrical measurements are almost universally made at the present time in terms of the international units as maintained by the several national laboratories.

2. Recent absolute measurements of the electrochemical equivalent of silver made in several countries differ somewhat among themselves, and therefore it is necessary to state explicitly what is the basis of any computations that one might make. This is not the case with the international units.

3. It is probable that the difference between the absolute electrochemical equivalent of silver and the value 1.11800 adopted for the basis of the international ampere is as small as the uncertainties in the atomic weights of silver and iodine which are involved in the computation of the Faraday.

A recent investigation at the Bureau has given for the electrochemical equivalent of silver 1.11804 mg per absolute coulomb. Hence, the absolute coulomb is 0.004 per cent greater than the international coulomb, or the faraday in absolute units is less by this amount. In absolute units the rounded off figure 96 500, seems the best value to assign, for the present, to this constant.

VI. COMPARISON WITH PREVIOUS INVESTIGATIONS

A. SILVER VOLTAMETER

The present results with the silver voltameter are most easily compared with past work by considering the values computed for the Weston Cell at 20° for the experiments in which the current was controlled. These experiments are called "absolute experiments" in Table 2. In Table 3 we gave the coulombs as calculated from the silver deposits and also from the measured current and time. We noted in the discussion of this table that the first method gave a lower value on the average than the second by $\frac{1.5}{100\,000}$ which is significant of the difference between the exact value for the cell 1.01827 recently found by the voltameter and the figure adopted for use by the international committee 1.0183 volts. It is evident then that the present work has given the value 1.01828_5 for the cell value. This is perhaps more readily seen by computing the cell value for each silver voltameter deposit in an absolute experiment and taking the mean. Having done this we find the average value from Smith's new form of voltameter to be 1.01828_9 and from the porous cup voltameter to be 1.01828_0 whence the result 1.01828_5 as given above. The value 1.01827 given as the result of previous work is based on 211 deposits made with the greatest care by Rosa, Vinal, and McDaniel. It thus appears that the present work agrees with the past to 0.0015 per cent.

B. IODINE VOLTAMETER

In their investigation Washburn and Bates made a preliminary comparison of the silver and iodine voltameters. The relation between their results and ours is more readily discussed in terms of the silver-iodine ratio than by means of the value for the faraday calculated from the iodine voltameter. This is because their value for the faraday involves Smith, Mather, and Lowry's absolute determinations using the filter paper voltameter. For the silver iodine ratio Washburn and Bates obtained the value 0.85045, which is 0.033 per cent higher than that recorded here. This difference is due to the fact that following the specifications of Smith, Mather, and Lowry, they employed the filter paper form of silver voltameter. Recent investigations at the Bureau of

Standards have shown conclusively that deposits obtained in such a voltameter are too heavy, because of the action of the filter paper. Hence, in order to compare the previously obtained ratio with that given here, it is necessary to compare the filter paper voltameter with those forms used in the present investiation.

The silver voltameters we employed were of the porous cup and nonseptum types. The electromotive force of the Weston normal cell at 20°, calculated from deposits made in such voltameters is 1.01827[19] volts. With the filter paper form the value 1.01866[20] was obtained; that is, the deposit in such a voltameter is about 0.038 per cent heavier than that obtained in the types used in the present investigation. Making the percentage correction to the silver iodine ratio determined by Washburn and Bates, the value 0.85013 is obtained, which agrees within 0.005 per cent with our final value. This agreement is probably in part accidental, since the filter paper voltameter is, in the hands of various investigators, scarcely capable of such reproducibility, and since in the previous investigation an accuracy better than 0.02 per cent was not claimed for the final value, which was founded on but four comparative runs. It does, however, confirm the belief that our results are not in error by more than 0.01 per cent.

VII. SUMMARY

We have made a careful comparison of the silver and iodine voltameters, using them in series so that the deposits of silver and iodine should be strictly comparable. The best procedure learned from previous investigations has been followed in each case. Our results are as follows:

1. Ratio of silver to iodine	0.85017
2. Electrochemical equivalent of iodine	1.31502
3. Value of the faraday (I=126.92)	96 515
4. Value of the faraday (Ag=107.88)	96 494
5. Value recommended for general use	96 500

Nos. 2, 3, and 4 are calculated on the basis of the international ampere, using 1.11800 mg per coulomb as the electrochemical equivalent of silver.

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[19] This Bulletin, 10, Reprint 220. (In press.)

[20] Ibid, 9, p. 197.

We are indebted to the University of Illinois for the use of part of the apparatus and materials for the iodine voltameter. These were loaned through the courtesy of Prof. Washburn, who cooperated with the Director and Dr. Rosa, of the Bureau of Standards, in making this work possible.

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PRODUCTION OF TEMPERATURE UNIFORMITY IN AN ELECTRIC FURNACE

By Arthur W. Gray

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The problems of modern science that demand nicety in the matter of temperature control are steadily becoming more numerous and more important. The requirements are, (1) to produce a sufficiently uniform temperature throughout the region to be used; (2) to maintain this for a sufficient time close enough to the particular temperature desired.

The difficulties of producing a uniform temperature throughout an extended region increase rapidly as the desired temperature departs from that of the room. Stirred liquid baths are generally troublesome at high temperatures. While the advent of the electric furnace marked a considerable improvement over previous methods of heating, nevertheless the temperature distributions within furnaces heretofore described indicate methods of control that are not altogether satisfactory.

It is the purpose of the present paper to set forth a method which has made it possible to heat a region of considerable length to any desired temperature up to about 700° C so uniformly that irregularities in the temperature distribution will be less than the effect of heterogeneity in thermoelements of the best quality, and probably less than the uncertainties at present existing in our knowledge of the temperature scale itself. The method has been applied to a furnace designed to heat uniformly bars under measurement for thermal expansivity, but the application of it clearly is not limited to problems of this general character.[1]

1. SOME FUNDAMENTAL PRINCIPLES UNDERLYING TEMPERATURE CONTROL

If a region in which no heat is generated or absorbed be surrounded by an isothermal envelope maintained constantly at the same temperature, all points within will ultimately come to this temperature. The approach to thermal equilibrium will be hastened by anything which increases the influence of radiation, conduction, or convection within the region. The main difficulty of the problem, then, reduces to that of securing such an isothermal envelope. When the temperature of the surroundings is fairly uniform and constant and is not far removed from the temperature desired, no great trouble is experienced. When such surroundings are not present, the logical procedure is to create them artificially as well as existing conditions will permit.

If the region in question has, by any suitable means, been heated uniformly to the desired temperature T, then any procedure which will eliminate heat loss or gain at every point of the surface will maintain T constant and uniform. The time rate dQ/dt at which heat will be conducted away from any portion of the bounding surface in consequence of a normal temperature gradient $-dT/dN$ and a thermal conductivity k in the surrounding substance, will be directly proportional to both dT/dN and k. Incasing the region in a poor conductor of heat will reduce the latter, and making the layer thick will reduce the former; but this procedure will not completely eliminate either of these factors. However, dT/dN and, consequently, dQ/dt can be made to vanish by supplying heat around the surface in such a way as to compensate exactly for the loss at every place. But the accurate regulation of such a supply presents difficulties which augment rapidly as T departs from the surrounding temperature, because the increased heat flow involved is subject to greater irregularities of surface distribution and to greater fluctuations with time. Conductivity parallel to the boundary, or the much more efficient action of a circulating fluid, will promote a uniform distribution of both the losses and the supply. The usual practice of abundant thermal insulation outside the source of heat will reduce variations in the losses, but not in the supply; but the effect that variations in either will produce upon the temperature of the region to be controlled can be materially lessened by the introduction of an insulating layer between the region and the source, since the mere separation of the two will reduce the already small dT/dN and also its rate of change $\frac{d}{dt}\left(\frac{dT}{dN}\right)$ at the surface of the former, while the reduction in k will still further lessen dQ/dt and d^2Q/dt^2. Whatever variations continue to exist near the region can be minimized by applying a small, properly regulated supply of heat around the surface, but best separated from it by an insulating layer, for the reasons just given. Since the addition of heat can usually be regulated more delicately than its removal, it is generally advisable to insure that the temperature of the main source of heat (the outside one) shall never exceed that of the region to be controlled.

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[1] Some results were communicated at the Washington meetings of the American Physical Society in December, 1911, and in April, 1913; and the more important features were outlined in a communication to the Washington Academy of Sciences. (A. W. Gray, J. Wash. Acad. Sc., 2, p. 248; 1912.) Since the publication of this paper the furnace has been improved and more data concerning its performance have been obtained.

2. PREVIOUS ATTEMPTS TO SECURE TEMPERATURE UNIFORMITY IN ELECTRIC FURNACES

Previous experimentors have tried to secure uniformity of temperature in an electrically heated air column by using the central portion of a long tube and by crowding the windings near the ends or other places where heat was lost most rapidly. In this way Daniel Berthelot[2] secured uniformity within 2° over the central 22 cm of a tube 85 cm long heated to 917°. Jaquerod and Perrot[3] in a well-insulated furnace without crowded windings heated a gas thermometer bulb 8 cm long with variations of less than 2° at 1066°. Waidner and Burgess[4] constructed a black body in which compensation for heat losses through the ends was secured in great measure by the use of a second independent heating coil surrounding the first and projecting 8 cm beyond each end. The winding of the secondary coil was very close about the ends and very open about the center. At 1245° this arrangement gave such remarkably uniform temperature that there was no variation of more than one or two tenths of a degree over a length of 12 cm. However, the method of varying the distribution of heat supply to compensate for lack of uniformity in the distribution of heat losses suffers from two serious defects: (1) It is a method of cut and try; (2) the proper arrangement to secure uniformity at one particular temperature does not give uniformity at any other temperature, necessitating a repetition of the cut-and-try process for every temperature desired. This is strikingly illustrated by one of the compensated black bodies used by Waidner and Burgess. While the temperature uniformity was practically perfect for 12 cm in front of the radiating diaphragm at 1245°, drops of 8°, 10°, and 11° took place within the second 4 cm of this same region when the diaphragm was at 621°, 1041°, and 1308°, respectively. This is shown graphically in Fig. 1, where the distribution obtained by Jaquerod and Perrot is also represented.

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[2] D. Berthelot: Ann. Phys. et Chim., 26, p. 119; 1902.

[3] A. Jaquerod and F. L. Perrot: Archives des Sciences Phys. et Nat., 20, pp. 45, 57; 1905.

[4] C. W. Waidner and G. K. Burgess: This Bulletin 3, p. 165; 1907.

The remarkable temperature uniformity exhibited by the black body used by Waidner and Burgess, is, however, an isolated example. It was obtained in one particular series of observations, at one particular temperature, and extended only for a short distance. The best results so far recorded in the way of heating a fair length at widely differing temperatures appear to be those obtained by Day and Sosman; and because they are the best that the writer has succeeded in finding, they will be referred to freely for purposes of comparison. The difficulties that Day and Sosman encountered in their attempts to heat uniformly a platinum-iridium bar 25 cm long, the linear expansivity of which they were determining, is best stated in their own words:[5]

> The problem of accomplishing this result gave us considerable anxiety. As has been stated above, the scheme of making optical measurements directly upon the bar without multiplying devices of any kind necessarily involves an opening in the furnace coil opposite each end of the bar, and a consequent cooling of that portion of the bar which is opposite the opening.[6] The amount of this cooling, which is greatest

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[5] In a paper by A. L. Day and J. K. Clement: Am. J. Science, 26, p. 425; 1908.

[6] These openings must be of sufficient size for good vision through them with a microscope. If too narrow, they are almost sure to produce such errors as arise from asymmetry of the light entering the objective and from inability to focus accurately. By using the suspended-wire method of measuring elongations (A. W. Gray, J. Wash. Acad. Sc., 2, p. 248; 1912. To be described in greater detail in an early number of this bulletin), the necessary openings may be reduced to narrow slits barely large enough to secure free motion to the wires, and these slits may be extended to the outside of the furnace by long tubes of the same cross section. In this way the disturbance of temperature caused by these openings may be rendered negligible, and at the same time the improvement in the optical conditions is considerable.

at the highest temperatures, reached a value of about 4 per cent in the first furnace coil (furnace I) which we wound. * * * Accordingly, another furnace coil (furnace II) was wound with the turns closer together near the openings. This changed the temperature gradient considerably without materially improving it, after which a third coil was prepared with still closer windings, which proved to be considerably overcompensated and was rejected. In all, we made five separate trials of this kind, in the last two of which (furnaces III and IV) a thick-walled iron tube was substituted for the porcelain furnace tube in the hope of gaining increased uniformity of temperature through the increased heat conductivity of the tube itself. This arrangement succeeded better, but we found it impossible so to arrange a winding that the temperature opposite the openings was uniform with that at the middle of the tube for all temperatures between 0 and 1000°. A winding which gave good results at the lower temperatures gave insufficient compensation at the higher ones. The obvious possibility of reaching a uniform distribution by subdividing the coil into sections in each

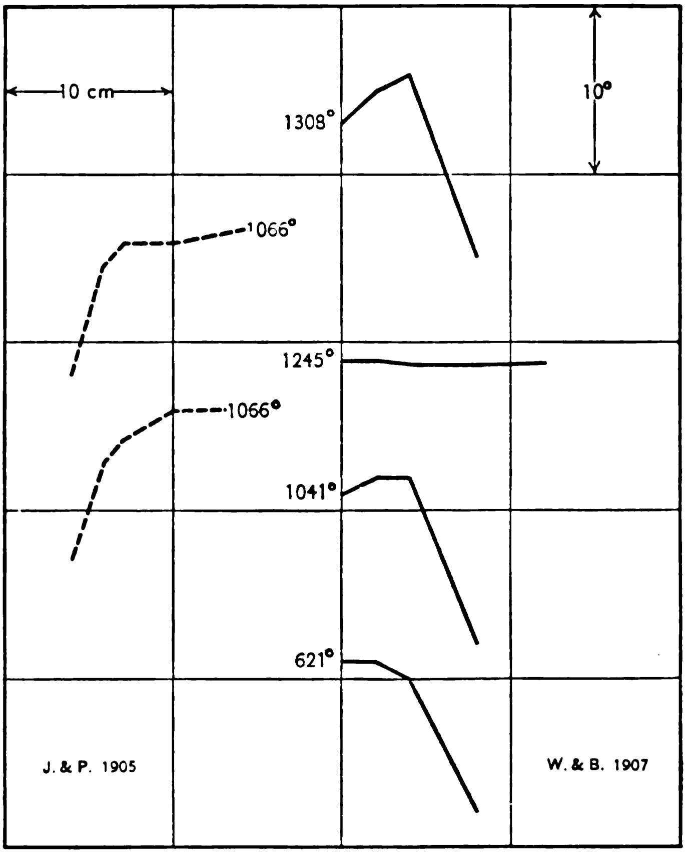

Fig. 1.—*Temperature distribution in the gas-thermometer furnace of Jaquerod and Perrot, and in a black body of Waidner and Burgess*

of which the current could be independently varied [7] was not tried on account of the cumbersome manipulation required, and in part also because the results which we obtained with considerable differences in the gradient appeared to agree very well among themselves.

Day and Sosman state that the deviations within the central 24 cm of their furnaces III and IV amounted to 5° at 300°, increasing steadily to about 20° at 700° and reaching about 50° at 1000°. While the thick-walled iron tube used in these latter trials produced markedly better results than the porcelain tube used in the earlier ones, still it is quite clear that even the conductivity of the iron was very far from adequate to secure uniformity, especially at temperatures much removed from the one at which a particular distribution of the heating coils gave the best results.

In a later paper [8] Day and Sosman describe a new furnace 70 cm long for determining the expansion of a 50-cm bar; but they give no data concerning the temperature distribution they secured. They merely remark that, since it was impossible to wind the furnace so as to give a perfectly uniform temperature along the bar, the furnace winding and consequent distribution of temperature were varied considerably for each run, in the hope of eliminating uncertainty from this cause in the average of all observations.

3. A METHOD OF REDUCING THE TEMPERATURE GRADIENT IN A LONG COLUMN OF HEATED AIR

In order to secure data that would aid in improving the design of electric furnaces suitable for expansivity determinations, especially in the direction of reducing the longitudinal temperature gradient, the writer studied experimentally the effect of various factors upon the temperature distribution within a long cylindrical air bath. A return-flow, oil-heated tube was used for the purpose of obtaining uniform lateral heating, so as to avoid confusing the observations by the effect of such irregularities as would be almost sure to exist in an electrically heated helix, no matter how carefully wound.

It is unnecessary here to enter into a detailed description of the many experiments made with this tube.[9] For our present purpose it will suffice to direct attention to a simple device in which the principles enunciated in the preceding sections have been successfully employed, viz, a plug formed of two thick blocks of a good heat conductor separated by a considerable layer of a poor conductor. For convenience the conducting blocks are united by a thin metal shell containing the insulator. Fig. 2 represents one in each end of the tube, the circumference of which is heated by a fluid circulating spirally around it and returning to the inlet end by linear flow through an outer concentric passage. In such a return-flow tube, the ends of which were plugged for 10 cm essentially as indicated, though not quite so well, an air column 4 cm in diameter and more than a meter long has been repeatedly heated by circulating oil to over 100° C so uniformly throughout its entire length that right against the plugs the temperature was only a few hundredths of a degree lower than in the center, while several centimeters farther inward the drop was only a few thousandths. Yet with the ends closed by equally long plugs of such heat insulators as cotton wool and cork there was a marked lowering of the temperature in the immediate vicinity within, even when the interior was only slightly warmer than the room; and in many of the experiments made this drop was apparent for a long distance within the tube. If the inside tube (of brass, 1 mm thick) were extended 4 cm beyond the heating jacket, relatively enormous end effects were produced in the air column, especially if the projections were not well pro-

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[7] This method, though resembling to a certain extent that to be described in the present paper, differs radically from it not only in constructional details but also in the fundamental principles involved.

[8] A. L. Day and R. B. Sosman: Am. J. Science, 29, p. 111; 1910.

[9] The writer is indebted to Mr. M. D. Hersey for assistance in carrying out this preliminary work.

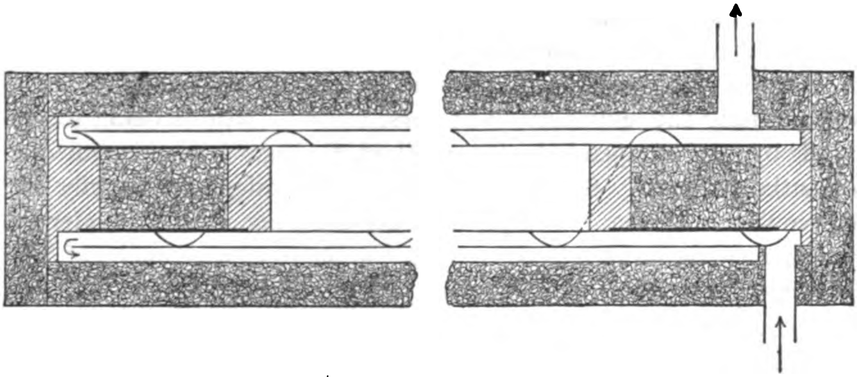

Fig. 2.—*Oil-heated return-flow tube, showing double plugs for reducing the temperature gradient*

tected by lagging. But unhindered radiation and conduction through the sides of the tube to the surrounding air was found to disturb the distribution of temperature within only slightly. In nearly all cases where the tube was not surrounded by an insulating jacket there was evidence of a small progressive drop in temperature in the direction away from the inlet and exit end. Doubtless this could have been made imperceptible by substituting a poorly conducting tube for the thin brass one separating the oppositely directed currents of heating fluid.

4. TRIAL APPLICATION OF THE DOUBLE PLUG TO AN ELECTRIC FURNACE

The double plug with small temperature gradient across an insulating layer described in the preceding section indicated a way of reducing such difficulties as were previously enumerated. Accordingly, an electrically heated furnace was constructed for determining the expansivity of bars, the elongations being measured by the suspended-wire method.[10] Fig. 3 represents the essential features. Since this furnace was designed primarily for convenience of manipulation and for securing merely moderate uniformity of temperature, only a partial use was made of the principles enunciated in section 1. The furnace tube, of iron fairly uniformly wound for its entire length with constantan ribbon, had its central portion completely filled with an iron block pierced by two longitudinal cavities, of square cross section, symmetrically situated above and below the geometrical axis of the tube. The lower cavity was almost completely filled by the bar to be measured, while the upper one contained a similar dummy bar, the temperature of which was determined by a thermoelement placed within a hole following the axis of the bar. While the conductivity of the large metal masses probably contributed considerably toward the production of temperature uniformity within this furnace, and while the smallness of the passages required for the suspended wires certainly prevented much disturbance, a very important feature of the whole construction was undoubtedly the type of plug used for closing the ends. This was essentially the same as the simple one described above, with the addition of an independent electrical heating coil wound in a groove within the outside conducting block. This coil made it easy to maintain the end at a temperature almost the same as that of the interior, thus reducing the longitudinal temperature gradient and thereby the outward conduction of heat. Suitably arranged differential thermoelements in the plugs, together with a convenient grouping of rheostats, made the temperature control an easy matter.

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[10] See note 6 on p. 454.

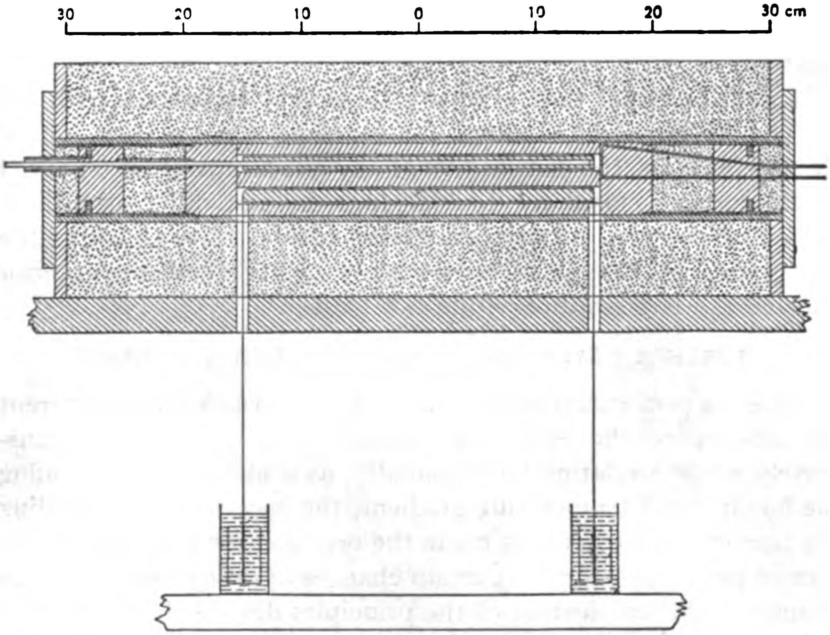

Fig. 3.—*First electrically-heated furnace for expansion measurements by the method of suspended wires, showing double plugs with outside blocks independently heated*

The furnace was built to accommodate bars 30 cm long. Examination of the temperature distribution throughout this length for various temperatures up to 684° C. showed that, if the outside end of the plugs was within 10° of the interior, no variation exceeding a few tenths of a degree occurred in the right-hand 15 cm except at the highest temperature to which the furnace was forced, when the extreme deviation was found to be 4°. Since the constantan ribbon burned out in the vicinity of the hottest place the next day, considerably before this temperature was again reached, it seems likely that this deviation was due to excessive local heating. The left-hand half of the bar did not, however, seem to be so uniformly heated as the right and was apparently consistently warmer, the maximum rise of 2° occurring in the second 5 cm from the left end. At the time this asymmetry was attributed to irregularity in either the heating coil or the insulation. Later, however, an investigation of the thermoelement used in exploring the temperature distribution disclosed sufficient heterogeneity to account for the apparent irregularity in both magnitude and location.

It is to be noted that, contrary to general experience with the method of crowded windings for reducing the gradient within electric furnaces, the distribution at any one temperature observed in the furnace closed by double plugs did not differ essentially from that observed at any other temperature. Even making the outer ends of the plugs considerably colder than the interior affected the temperature within but little.

5. FURTHER DEVELOPMENT OF THE ELECTRIC FURNACE

Since the performance of the trial electric furnace made apparent the efficacy of the end-heated double plug, conducting transversely while insulating longitudinally, as a means for controlling the longitudinal temperature gradient, the necessity for rewinding the burned-out heater was made the occasion for remodeling into a more permanent form. Certain changes in design were made to secure a fuller application of the principles discussed in section 1. Other changes facilitated manipulation and investigation. Fig. 4 is a photograph of the new furnace and of the comparator as arranged for expansion measurements. Fig. 5 shows in section the more important features. For the sake of clearness minor structural details, as well as the bars and thermoelements, have been omitted.

The iron tube of the trial furnace, together with its contents, is retained without essential alteration. The principal change consists in removing the heating coil from the tube A, upon which it had formerly been wound, and substituting two independent concentric heaters (wound on the iron pipes B and C) to supply heat uniformly for the entire length of the interior. In the experi-

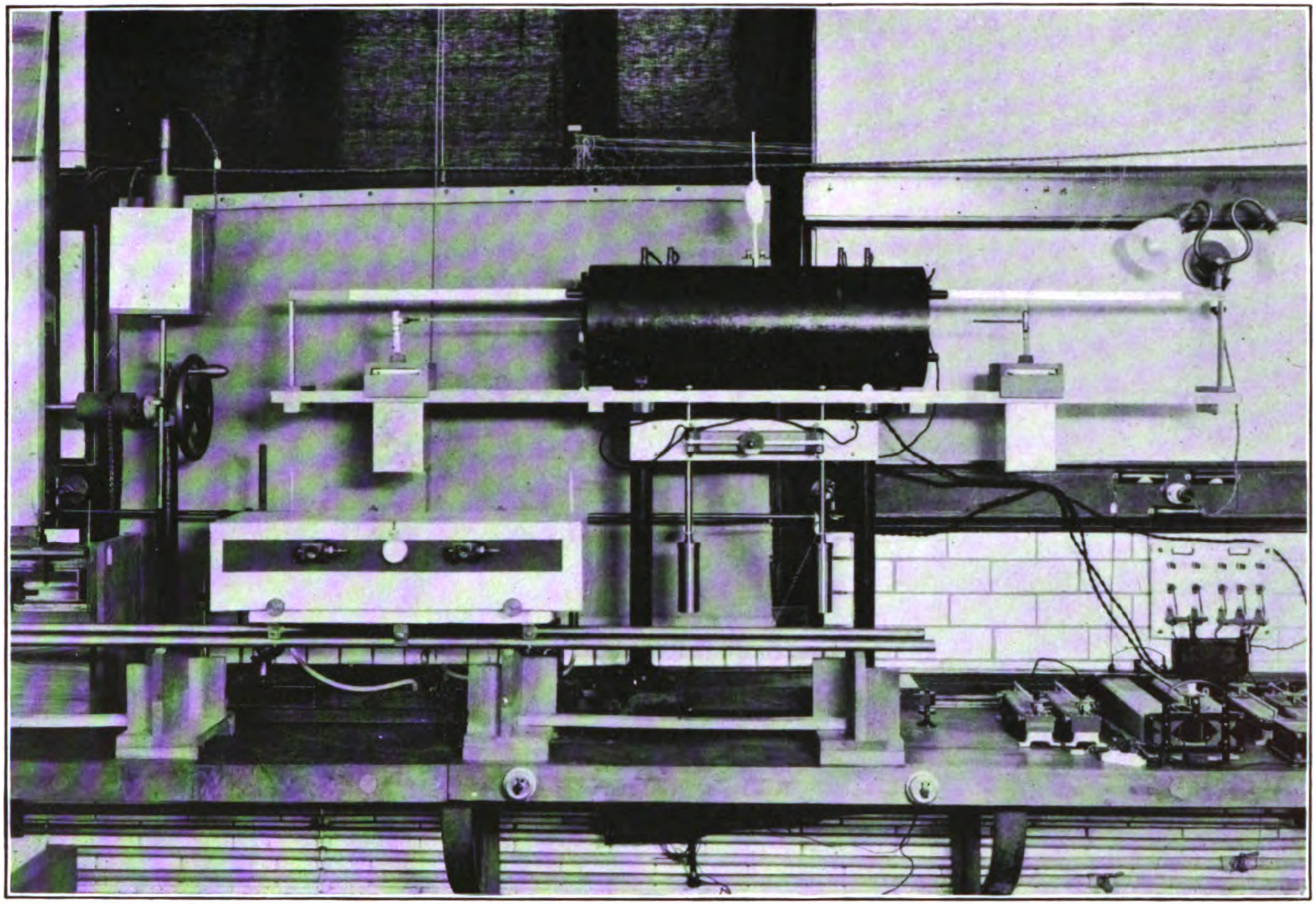

Fig. 4.—*Second electric furnace and comparator as arranged for expansion measurements*

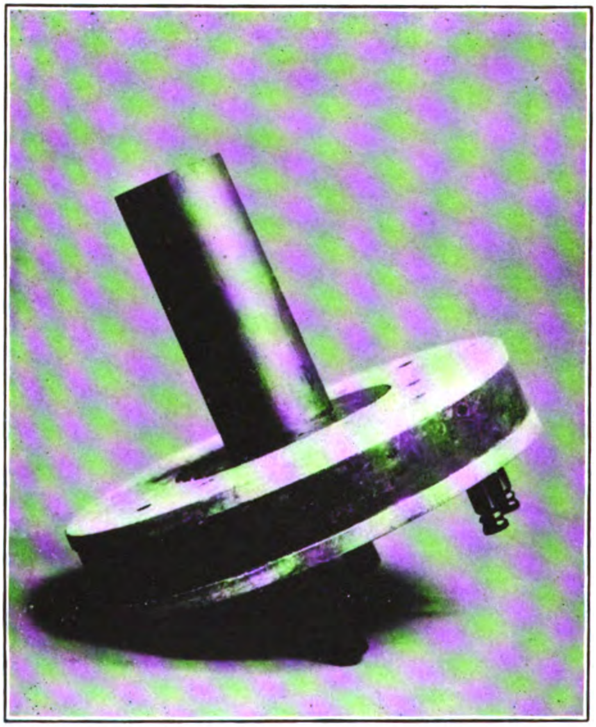

Fig. 6.—*A double plug with flat end-heating coil*

ments so far made, air has formed the insulation filling the annular spaces between A and B and between B and C, except for some layers of mica and of asbestos cloth, in all about 4 mm thick, wrapped tightly around the heating ribbon on B. C is covered in the same way, and then the surrounding space to the pipe D, which forms the outer shell of the whole furnace, is filled with asbestos-magnesia compound. Both of the end plugs are pierced by tubular openings for inserting thermoelements within the dummy bar. Large insulating heads, each composed of two disks (E, F and E′, F′) of 1 cm asbestos building lumber separated by 3 cm of asbestos-magnesia compound, fill the whole cross section at the ends of the casing D and reduce heat losses. These heads are rigidly attached to the double plugs, and carry binding posts leading to the heating coils, as well as handles to facilitate insertion and removal. In most of the experiments with this furnace heat was supplied to the plugs by means of the coils described in section 4 and illustrated in Fig. 3. Recently, for reasons that will appear later, the coils filling the grooves in the blocks G and G′ were cut out of action, and two new coils H and H′ were substituted. These are flat coils of the same diameter as the tube C, against the ends of which they bear. Space for them was provided by removing the central portions of the disks E and E′. One of the remodeled plugs is illustrated by the photograph Fig. 6.

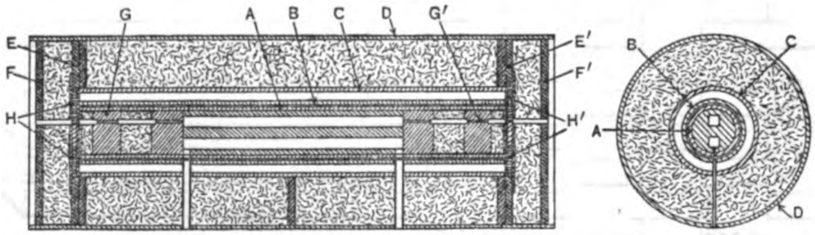

Fig. 5.—*Section of second electric furnace, showing more or less diagramatically the more important features*

The heaters that cover the pipes B and C are of nichrome ribbon wound longitudinally instead of helically. The construction is indicated in Fig. 7. A flat mat is made of the resistor ribbon and strips of micabeston [11] woven together in basket fashion. This is wrapped about the heater tube (previously covered with a layer of micabeston), and the opposing ends of each insulating strip are lapped for a short distance and tucked under alternate lengths of the ribbon. Then follows another layer of micabeston, and, finally, a wrapping of asbestos cloth. As each layer is applied it is drawn down firmly by a tight helical bandage of cotton tape, which is removed as soon as the layer has been cemented in place by warming and then cooling the tube. The final wrapping of asbestos cloth is secured by a bandage of nichrome ribbon. The lengths of ribbon bounding each edge of the mat and the two on either side of the middle are left long enough at one end to serve as electrical terminals. When the heater is wound, these terminals come out at opposite ends of a diameter at one extremity of the tube, and they connect the two halves of the winding in parallel. Each pair of large binding posts seen on top of the furnace in Fig. 4 leads to one of the concentric heaters. After a heater is wound, current is passed through it until it is thoroughly baked to remove all the resinous cement.

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[11] An insulating preparation of mica flakes and a resinous cement pressed into large, thin, flexible sheets.

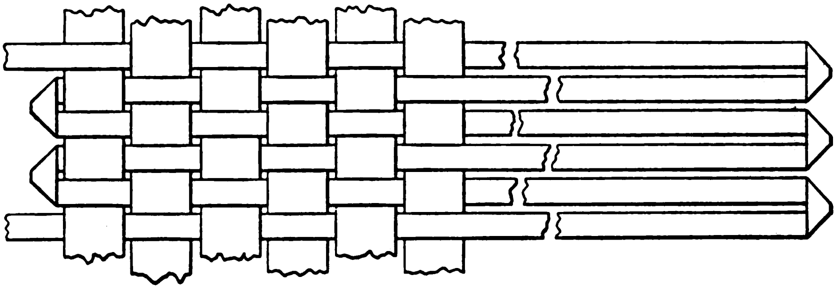

Fig. 7.—*Diagram of furnace winding*

This method of winding possesses the following advantages: (1) Any irregularities in the resistance of the heating ribbon are distributed in such a way as to produce a minimum effect upon the longitudinal distribution of temperature; (2) the winding is non-inductive; (3) the maximum difference in electrical potential that can occur between adjacent portions of the winding is limited to the drop in a length of ribbon twice as long as the furnace. This makes the danger of arcing by accidental contact considerably less than in the ordinary form of noninductive winding;

(4) if adjacent windings should accidentally touch, only a short length of ribbon could be short circuited; (5) spaces for the side openings down which the length-defining wires are suspended can be provided without affecting the heat supplied per unit length of the furnace tubes; (6) the location of the terminals combines both convenience and safety.

A furnace of the type here described requires considerable time to attain thermal equilibrium. The lag, however, causes no great inconvenience, because in any precise expansion determinations sufficient time should be allowed for the specimen to reach mechanical equilibrium; that is to say, for all unbalanced internal stresses to disappear. The gain in temperature uniformity and constancy more than counterbalances any time lost from avoidable lag. Nevertheless, it seems likely that a furnace amply sufficient for most purposes could be made with considerably less lag. In this connection it might be mentioned that the principal use of the inner concentric heater is to hasten the attainment of approximate thermal equilibrium. Experience has shown that when the proper adjustment has been secured, the steadying action of the insulation within the outer heater is sufficient to wipe out fluctuations in both losses and supply of heat.[12]

6. DETERMINATION OF TEMPERATURE AND TEMPERATURE DISTRIBUTION

It was convenient and sufficiently accurate to determine all temperatures within the furnace described in section 5 by means of $Pt-PtRh$ thermoelements. These were all made from the same spools of the highest purity Heraeus wire and did not show sufficient heterogeneity to cause inconvenience. One element kept as a reference standard was calibrated by the heat division of this Bureau at the freezing points of copper, silver, antimony, and zinc, and at the boiling points of naphthalene and water. Two others, conveniently mounted within sealed protective casings, were used in the actual determinations, one entering each end of the furnace. The arrangement and the temperature control of the furnace were such as to afford favorable conditions for intercomparison.

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[12] The use of two concentric heaters bears some resemblance to the cascade furnace described by Harker (Proc. Roy. Soc., A, **76**, p. 237; 1905) for reaching a temperature of about 2000° in a heater tube made of the same material as Nernst lamp glowers. To avoid the necessity of having contacts on this tube capable of carrying relatively large currents, and the consequent severe stress on the parts, it was surrounded by a coil of nickel wire heated by an independent circuit to about 1000°, and insulated from the inner tube by a layer of zirconia. No precautions seem to have been taken to secure uniformity of temperature within.

A photograph of a protected thermoelement is shown in Fig. 8. The furnace end is encased in a horizontal glazed porcelain tube 4 mm external diameter and 500 mm long, closed at the junction end. Within, the wires are separated in the usual way by an unglazed porcelain capillary. The junctions with the copper leads are at the bottom of a vertical glass tube, joined to the porcelain tube by a tee of brass and thin copper tubing, which permits a slight amount of bending. The copper leads reach the outside through a second glass tube within the first. Reserve platinum and platinum-rhodium, to allow for the occasional removal of contaminated ends near the furnace junction, or for lengthening the elements is carried in the form of an open helix coiled around the inner glass tube and bound down with wrappings of thin silk, the cold junctions being located near the bottom, but on the outside of the inner tube, so as to be close to the outer one, which was drawn down thin in this region. All wires and wrappings within the glass tube are thoroughly imbedded in melted paraffin. This mounting furnishes a protection against furnace vapors and electrical leakage along moisture films, and has been found much more convenient than the loose wires formerly used. In Fig. 4 the thermoelement just described appears in position, extending into the right-hand end of the furnace. Another, mounted in much the same fashion, appears at the left. The temporary containers for the ice bottles, which are small cylindrical Dewar flasks surrounded by cotton wool, can be seen hanging from wooden slides that rest upon the long steel track. The millimeter scales above the track indicate the positions of the junctions within the furnace.

A thermoelement with its cold-junction temperature given by a mercurial thermometer extends through the furnace casing and rests against the outer cylindrical heater. A differential element, connected to the binding posts on top of the furnace, indicates difference in temperature between the outer and the inner heater. Another in the left plug gives the difference between the axis and the circumference of the inner end. Still another, added since

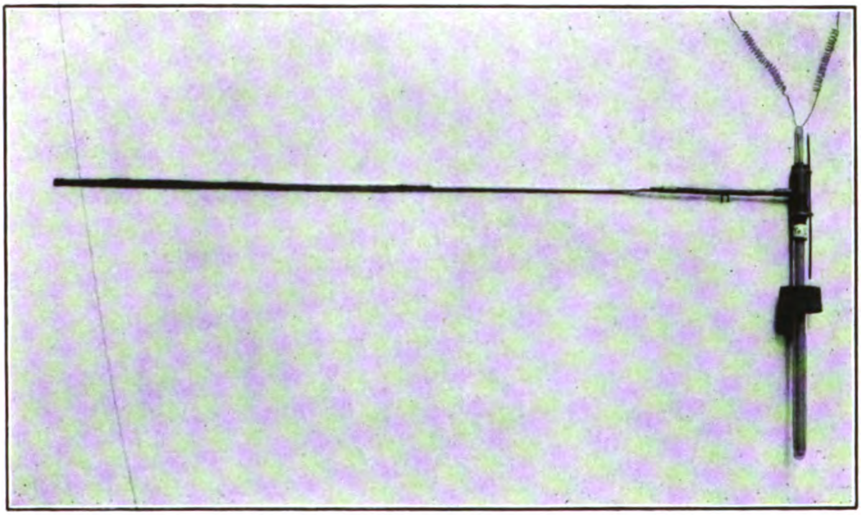

Fig. 8.—*A protected thermoelement*

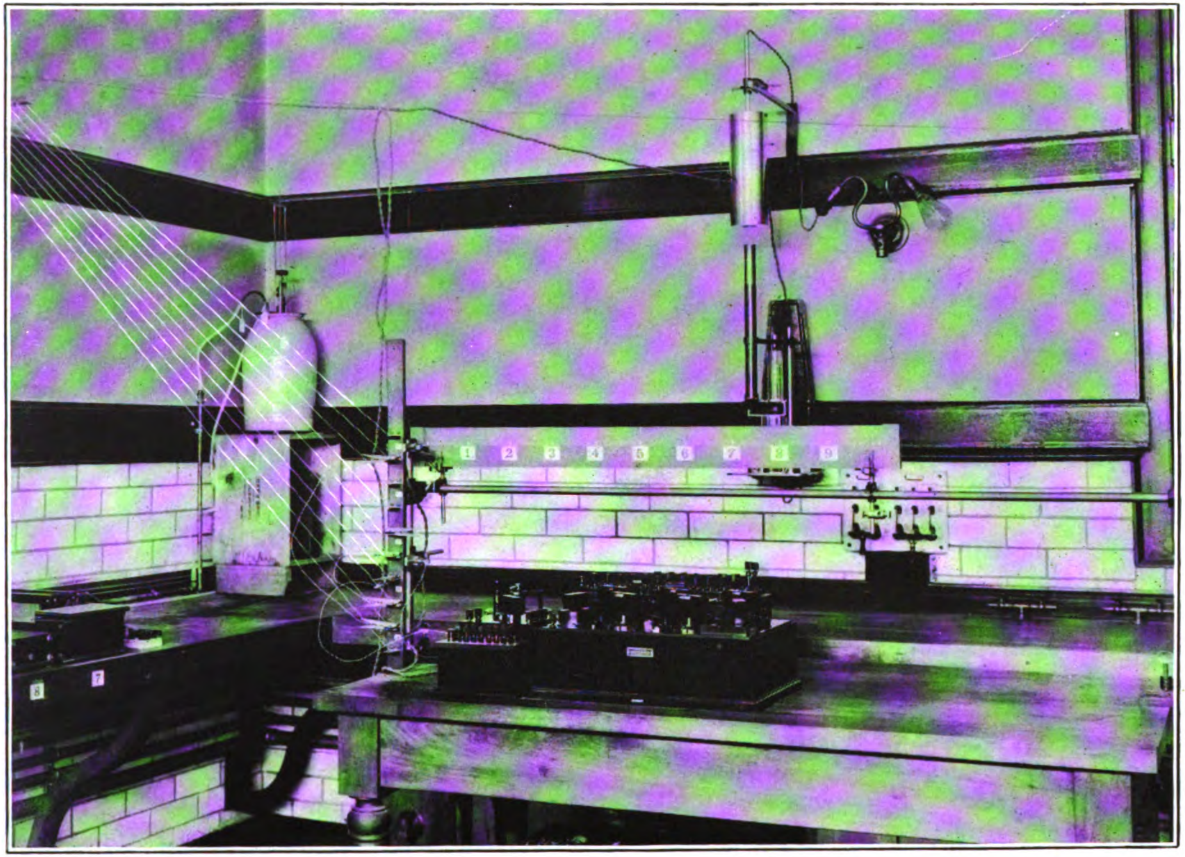

Fig. 9.—*Potentiometer and galvanometer*

the photograph was made, indicates the difference between the end-heating coils H and H′, Fig. 5.

The electromotive forces are measured by a five-dial Diesselhorst potentiometer[13] made by Otto Wolff and calibrated by the electrical division of this Bureau. The galvanometer, of the Jaeger low-resistance type[14] made by Siemens and Halske, was sufficiently sensitive when critically damped to give a deflection of about 2.5 mm per microvolt on a scale 1 meter distant. All galvanometer wires, as well as the potentiometer and storage battery, were insulated from metal equipotential shields connected to earth through the laboratory water pipes. No irregularities have been noticed even on very moist days.

The general arrangement of the galvanometer illumination is shown in Fig. 9. It is similar in principle to some of the devices on the market, but surpasses them in brilliancy of illumination and sharpness of image. The source of light is a General Electric Co.'s concentrated filament, tungsten projection lamp, which is surrounded by a nickel-plated brass tube open at the top and closed at the bottom except for a 4-cm central hole. The light coming through this opening traverses a vertical telescoping tube, at the bottom of which is a right-angled total reflecting prism for directing it on the galvanometer mirror, whence it is reflected to a Hartmann and Braun lightly frosted glass millimeter scale. At the top of the telescoping tube is an ordinary plano-convex lens, which serves as a condenser and forms an image of the lamp filament on the galvanometer mirror. Just below the condenser is a metal screen with a rectangular opening across which the index extends. This is formed of a piece of wire one-thirtieth mm in diameter stretched between two short pieces of larger wire, which have been filed to pointed half cylinders so as to obtain sharply defined edges. An achromatic lens just above the reflecting prism forms on the glass scale an enlarged image of the opening and index wires. The images of the larger, pointed wires stand out so clearly on the brilliantly illuminated field (about 17 by 50 mm) that their position can be read within a few millimeters by a person eight or ten meters distant even in a well-lighted room, while the image of the fine wire permits estimation to a tenth of a millimeter when the observer is close to the scale.

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[13] H. Diesselhorst: Zs. f. Instrk., 28, p. 1 and p. 38; 1908.

[14] W. Jaeger: Zs. f. Instrk., 28, p. 206; 1908.

All observations of temperature within the furnace involved the use of both the thermoelements entering it through the ends. The junction of the right-hand element was placed at the center of the dummy bar, with the junction of the left about 2 mm away, which was as close as the porcelain protecting tubes would permit the junctions to approach each other. The emf of the right element alone was read; also that of both connected in opposition. When making an observation both the emf to be measured and the potentiometer current were reversed and returned to their original directions by means of the oil immersed commutator that accompanies the potentiometer.

To explore the distribution of temperature within the furnace, one thermoelement was located so that the tip of its porcelain protecting tube could be just touched by that of the other when inserted as far as possible. The two elements were connected in opposition. The warm junction of the second was slowly moved through the furnace by sliding the container of the ice junction along its track while galvanometer deflections were noted for various positions. Check readings were taken at several points passed in opposite directions. In the same way the other end of the furnace was explored with the second element fixed while the first was moved. The paths traversed by both junctions overlapped for the central 20 cm of the furnace. This procedure also yielded comparisons of the thermoelements with three different depths of immersion for each. One millimeter change in deflection indicated a change in temperature of between 0.058° and 0.086°, depending on the temperature. The sensitivity exceeded the reliability attainable with thermoelements of even the best quality.

7. DISTRIBUTION OF TEMPERATURE IN THE IMPROVED ELECTRIC FURNACE

The distribution of temperature was first investigated when the end heating was supplied through the coils in the blocks G and G′ (see section 5 and Fig. 5), and before the central portions of the asbestos lumber disks E and E′ had been cut out to make room for the flat coils H and H′. All of the numerous curves obtained showed the characteristics of the two reproduced in Fig. 10. The circle on each curve indicates the middle of the furnace. The points 30 cm on either side were 1 cm within the extremities of the furnace tubes, which were 62 cm long, the length of the casing being 74 cm. The most striking features of the temperature distribution are the steep gradient beyond the heated blocks and the drop of several degrees just within them. This drop was evidently due to heat losses at the ends caused by radiation or air currents, or both combined, through the annular spaces between the concentric tubes. As will be seen presently, it disappeared completely after installing the coils H and H′ and at the same time closing the ends of the annular spaces with 1 or 2 cm of asbestos.

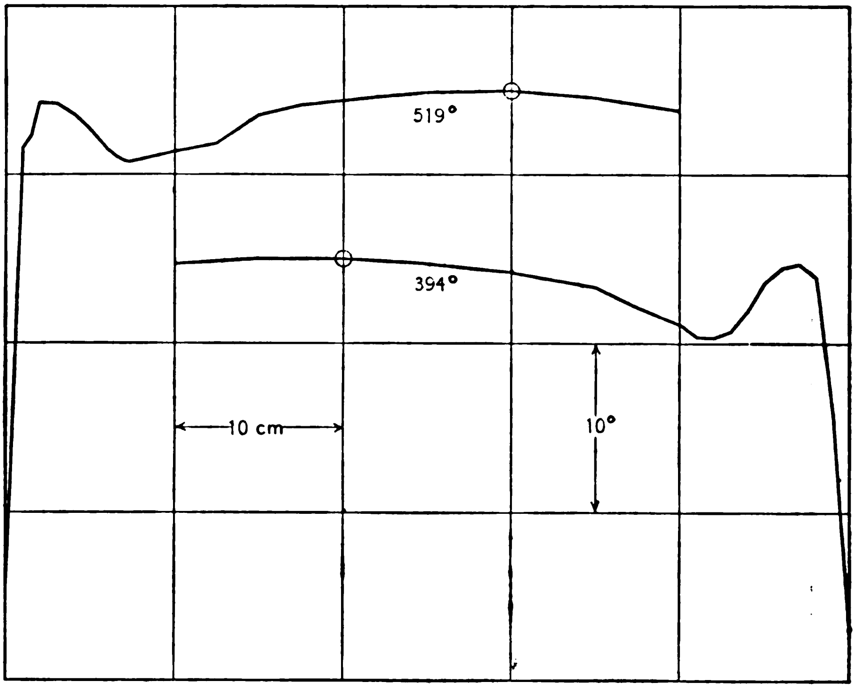
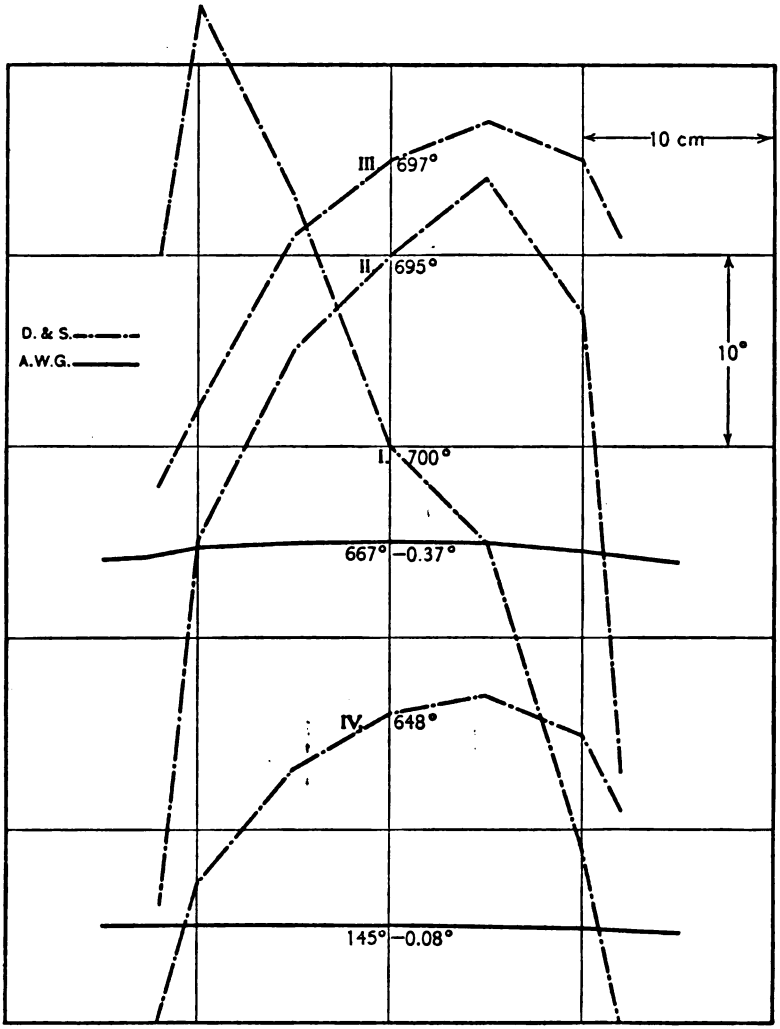


Fig. 10.—*Characteristic distributions of temperature in the seccond electric furnace before installing the flat end-heating coils. The small circles indicate the center of the furnace*

However, in spite of the internal drop, fair uniformity throughout the central 30 cm for which the furnace was designed could be easily obtained by merely raising somewhat the temperature at the ends. Fig. 11 presents two examples to show that good per-



formance is not limited to some particular temperature, as we have seen to be the case with furnaces in which adjustment of the

Fig. 11.—*Distributions of temperature throughout the central 30 cm of the furnace shown in Figs. 4 and 5 obtained at 145° C. and 667° C. under conditions shown in Fig. 10. For comparison, temperature distributions obtained by Day and Sosman throughout the central 24 cm of four different furnaces are plotted on the same scale*

distribution is attempted by the ordinary cut-and-try method of crowding the windings near the ends. At 667° the mean temperature throughout the full 30 cm was 0.37° lower than the temperature at the center, with a maximum drop of 1° at the extreme ends of the interval; at 145° the mean temperature over the same region was 0.08° lower than at the center, with a maximum drop of 0.25° at the extreme ends. For purposes of comparison with the best previous work (see section 2) the distributions recorded by Day and Sosman in four of their furnaces at temperatures nearest to 667° are reproduced in the same figure. These are plotted on the same scales as the writer's curves, for both length and temperature, but cover only 24 instead of 30 cm.

As an indication of the constancy attainable, it might be mentioned that during the 20 minutes that passed while the observations at 667° were being made the temperature at the center rose 0.067°, or at the rate of 0.2° per hour. During this period no attention whatever was paid to regulation of the heating currents. From the way in which the furnace always behaved it was clear that even better control as regards both constancy and distribution could have been obtained merely by more careful adjustment.

Some experiments were made to determine the temperature distribution when heat losses at the ends were reduced merely by the action of the double plug without supplying any heating current to the coils in the end blocks. Two typical results at widely differing temperatures are shown in Fig. 12. In this (and also in Fig. 13) the full lines to the right and the dash lines to the left represent explorations with two different thermoelements. Perfect agreement in the region where both overlap is not to be expected; partly because of slight heterogeneity in the elements; partly because some points investigated with one are passed over with the other, and because moving a thermoelement into the furnace disturbs the gradient slightly, especially if not done very slowly. The dotted lines represent on the same scale the results obtained by Day and Sosman with the method of crowded windings, the roman numerals designating the furnaces, and the temperatures being those at the center.

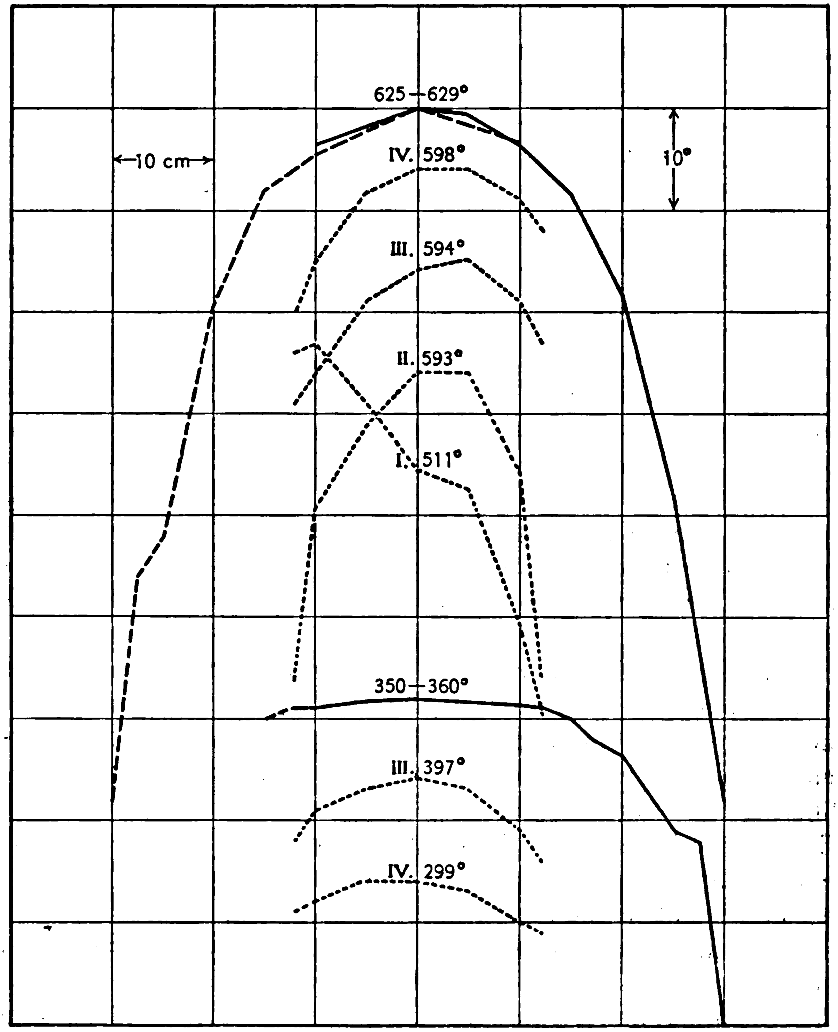


Fig. 12.—*Distributions of temperature obtained by using the double plugs without supplying any heating current to the coils in the end blocks. The dotted lines represent the results of Day and Sosman at neighboring temperatures, who attempted to compensate for the losses by the method of crowded windings*

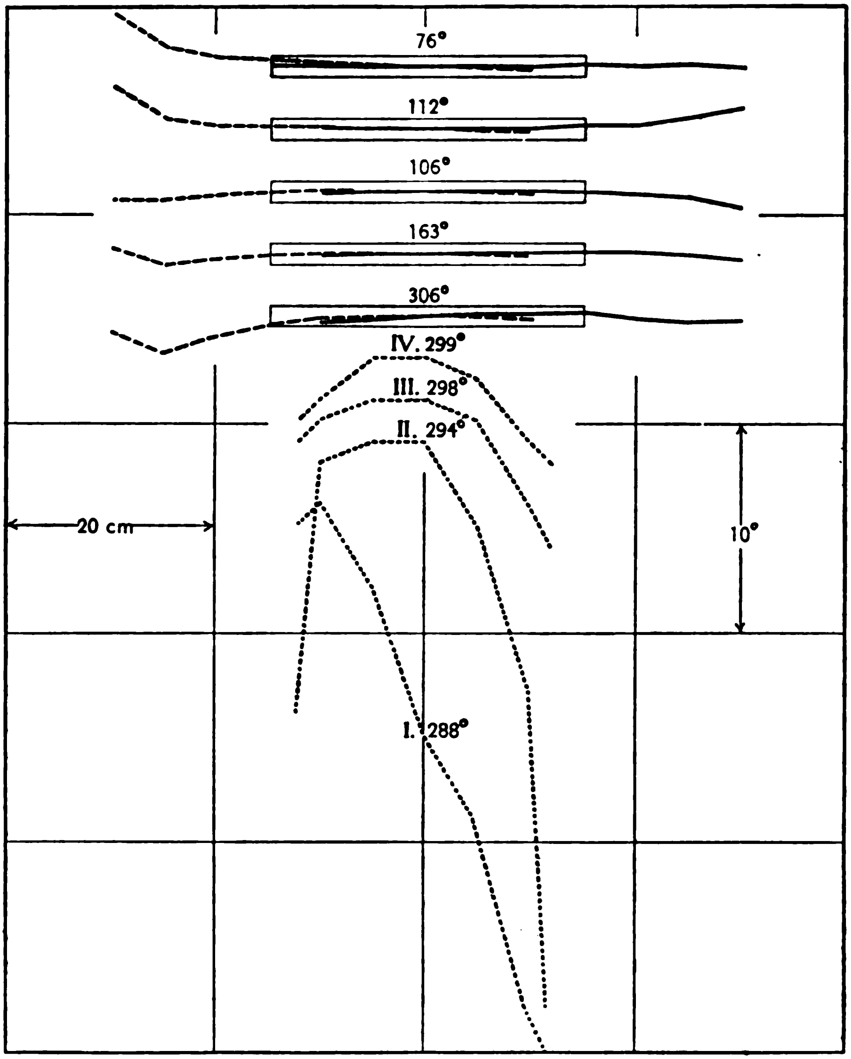


Fig. 13.—*Distributions of temperature obtained after installing the flat end-heating coils. The length of each rectangle represents the 30 cm occupied by the specimen; the height represents one degree. The distributions are given for a total length of 60 cm. The dotted lines below indicate on the same scale distributions obtained by Day and Sosman over 24 cm*

Fig. 13 is now presented to show the effect of heating the ends by means of the flat coils H and H′, G and G′ serving merely as transversely conducting blocks. At the top of the figure are represented the results of the first five consecutive runs after the flat coils were installed. The length of each rectangle represents the 30 cm occupied by the specimen; the height represents 1°. The temperature distributions are given for a total length of 60 cm. For comparison distributions obtained by Day and Sosman over 24 cm are placed below.

In every temperature distribution represented at the top of the figure it will be noticed that to the right of the center the full line lies above the dash line, while to the left the reverse is the case. This same peculiarity was also exhibited by all the distribution curves of later experiments, regardless of whether the exploration with the right thermoelement preceded or followed that made with the left. This would suggest that the small divergences in the two explorations at each temperature are to be ascribed, at least in part, to heterogeneity in the thermoelement wires.

To get the best results the furnace is capable of yielding, it is necessary to adjust both end coils rather closely to the temperature at the middle and to maintain the adjustment long enough to reach equilibrium. This is somewhat troublesome with only two thermojunctions for three positions, because pushing a cold porcelain tube rapidly into the furnace disturbs the temperature distribution a little. Fig. 13 shows evidences of lack of adjustment and of failure to reach equilibrium, especially in the left half. This is because the final adjustment was usually made with the left thermojunction at the center, while the right one was near the end coil, the left end being allowed more or less to shift for itself. Since the measurements represented by Fig. 13 were made, the stationary differential thermoelement mentioned on page 465, with a junction near each end coil, was added to facilitate the adjustment. A sensitive detector indicating temperature changes close to the main heater would aid in maintaining constancy during the time the potentiometer is being used for the measurements proper. The results exhibited were obtained with a single galvanometer in the regular course of expansion determinations.

That no unusual effort is required to obtain fair uniformity of temperature is shown by the table below, which represents 16 consecutive runs made while determining the expansivity of a bar of invar. Alongside the temperature observed at the center is recorded the correction that must be added to obtain the mean temperature throughout the 30 cm occupied by the bar. In many of the runs the heating currents required to maintain the desired temperature were estimated and switched on late in the afternoon. The furnace was then left to itself overnight. The temperature distribution found the following morning was explored and used. Reference to the table shows that in only one case (and that under known unfavorable conditions) did the mean temperature differ by more than 0.16° from that at the center.

Temperature Distributions in Consecutive Trials of the Electric Furnace Shown in Figs. 4 and 5

Temperature	Correction	Temperature	Correction	Temperature	Correction	Temperature	Correction
°	°	°	°	°	°	°	°
390	−0.16	242	+0.13	233	−0.10	445	−0.25
393	−0.13	170	−0.04	214	−0.05	294	−0.05
278	−0.03	188	+0.04	344	−0.05	262	+0.03
271	+0.03	207	−0.10	314	−0.10	175	+0.15

WASHINGTON, February 3, 1914.

THE SILVER VOLTAMETER—PART IV

THIRD SERIES OF QUANTITATIVE EXPERIMENTS AND SPECIAL INVESTIGATIONS

By E. B. Rosa, G. W. Vinal, and A. S. McDaniel

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I. INTRODUCTION

In the three papers [1] preceding this the course of the work has been traced from its beginning in 1908 until the International Technical Committee met at the Bureau of Standards in April, 1910, to carry out a joint investigation of the voltameter and to determine the voltage of the Weston normal cell. The experiments that disclosed the cause of difference between the porous-pot and the filter-paper voltameters have been described. The causes for different forms of deposit and the chemical reactions taking place in the electrolytes contaminated by filter paper and similar substances have been discussed, and methods of preparing the electrolyte with tests for judging its purity have been developed. Finally, the reliability of the porous-pot form of voltameter as a standard for the measurement of electric current has been established. Our part in the work of the International Technical Committee is detailed in the report of that committee, which has been published.[2]

At the conclusion of the joint work some further experiments were deemed necessary, since the specifications for the voltameter had not been agreed upon and a number of outstanding questions required answers before official specifications could be prepared.

The agreement of the different types of voltameters used by the delegates had been sufficiently good, however, to enable the committee to fix the voltage of the Weston normal cell as 1.0183 volts at 20° C.

The porous-cup voltameter and a new form devised by Mr. F. E. Smith, of the National Physical Laboratory, England, had been found to be in particularly good agreement. This latter form has no septum between the anode and cathode except for a glass trap to catch the slime of the anode.

The object of the work described in this paper was, therefore, to carry out a series of experiments on these two forms of voltameters that should afford as complete data as possible for formulating specifications, according to which the voltameter might be used at any time for the measurement of current and (in connection with resistance standards) for checking the constancy of the Weston normal cell. This work consequently included not only a further comparison of these two forms of voltameters, but also a study of the effects of traces of uncombined acid or of base in the electrolyte, and of variations of other conditions.

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[1] This Bulletin, 9, p. 151 (Reprint No. 194); p. 209 (Reprint No. 195); p. 493 (Reprint No. 201).

[2] Report of the International Technical Committee, 1912.

II. DETERMINATION OF THE VOLTAGE OF THE WESTON NORMAL CELL

The International Technical Committee fixed the voltage of the cell to five significant figures (1.0183 at 20° C), but it is desirable to reach an accuracy sufficient to justify recording six figures. It has been our practice in the present work to give the result of each experiment as a determination of the voltage of the Weston cell rather than to assume the latter and compute the electrochemical equivalent of silver. The International Electrical Congress of 1908 defined the electrochemical equivalent of silver to be 1.11800 mg per coulomb, and we have based the calculation of the emf of the Weston cell on this value. The absolute value of the electrochemical equivalent as recently determined by the present authors in conjunction with Rosa, Dorsey, and Miller,[3] at the Bureau of Standards, using the porous-cup and new form of voltameters and an absolute current balance, is very close to this figure, namely, 1.11804 mg per coulomb. The voltameter determinations on which this is based form part of the observations included in this paper, the others being made subsequently. The mean value which we give in this paper for the Weston cell at 20° C is only 8 parts in 1 000 000 higher than that recorded in the paper of Rosa, Dorsey, and Miller. It would appear from this data, therefore, that the absolute electrochemical equivalent of silver is about 1.11805, assuming that no significant change has occurred in the concrete standards for the ohm and the volt since the balance work was discontinued and assuming that the inclusions of foreign material in the deposited silver are negligible. We shall discuss the latter point somewhat further on in this paper.

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[3] This Bulletin, 8, p. 367 (Reprint No. 171).

A. BASIS OF REFERENCE FOR CURRENT AND VOLTAGE MEASUREMENTS

1. WESTON NORMAL CELLS

In the first paper of this series the arrangements for preserving four standard cells at a constant temperature were described. For practical work we have used one of these, cell No. 109, and by means of the other three and a large number of reference cells of the Bureau have carefully determined the relation of this cell to the mean Weston normal cell, which was defined[4] by the International Technical Committee. Throughout the present paper the value recorded for each experiment has been reduced to this basis by adding to the number actually computed from the electrolysis experiment a correction which expresses the amount by which the voltage of cell No. 109 was lower than the mean Weston normal cell. This correction was usually about 25 millionths of a volt, but varied by a few millionths from time to time.

2. RESISTANCES

The formula for the emf of the cell is $E = \frac{MR}{1.11800t}$ where t is the time of the deposit in seconds, M the mass of silver deposited in milligrams, and R the value of a resistance standard across which the fall in potential is maintained equal to the voltage of the cell.

We have used in our recent work, as before, a resistance standard of 2 ohms, number 2342, made by Otto Wolff, and have assigned to it a value in international ohms in accordance with the definition given by the International Technical Committee.[5]

B. MEANING OF THE TERM "INTERNATIONAL VOLTS"

Our results, therefore, express the voltage of "the Weston normal cell" at 20° C in terms of *international volts*. It should be noted here that a slight ambiguity may arise as to the meaning of the term "international volts," and hence in some cases it will be necessary to state explicitly what is meant.

In accordance with the decisions of the London conference the silver voltameter is to be used to measure the international ampere, and this in connection with the international ohm may be used to measure international volts. On the other hand, a standard cell whose voltage is expressed in terms of the mean Weston normal cell taken as 1.0183 volts at 20°C, is now the recognized method of measuring international volts in accordance with the recommendation of the International Committee on Electrical Units and Standards. The difference between the two measurements will be the same as the difference between the round value 1.0183 volts recommended by the International Committee, and adopted for use by the several countries and the more exact figure expressing precisely the value found by means of the silver voltameter and a standard resistance, assuming that the errors of measurement are negligible. From a long series of determinations with the voltameter we believe that this difference is about 3 parts in 100 000. (See p. 486 below.) However, for the present at least, the value 1.0183 should always be used in practice rather than the value given in this paper, 1.01827. In other words, the international ampere in practice should be derived from the ohm and volt (the latter being fixed by the Weston normal cell taken as 1.0183) rather than from the silver voltameter. This fact, however, does not lessen the significance of the results obtained in this paper, since one of the most important objects at present is to be able to write specifications for the voltameter and to confirm the decision of the International Committee.

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[4] The Weston normal cell was defined as the mean of the cells submitted by the National Physical Laboratory, The Laboratoire Central d'Électricité, the Physikalisch Technische Reichsanstalt, and the Bureau of Standards, taken by groups. In the recent paper of von Stienwehr (Zs. f. Instr., 33, p. 321) the French laboratory was not mentioned in this connection. (International Technical Committee report, p. 8.)

[5] International Technical Committee report, p. 8.

C. VOLTAMETERS AND MATERIALS

In the first paper [6] the porous-cup voltameter and also the Poggendorff and siphon forms, which we have continued to use in the present work, have been described and illustrated. Beside these we have made use of two other forms, which we briefly describe here. The one which we have designated as the modified siphon consisted of a small glass dish 4.5 cm in diameter and 3 cm deep which was submerged in the electrolyte. From the top edge of this dish there projected upward four short glass rods that supported an annular siphon whose lower edge was just below the surface of the electrolyte. A cross section of this voltameter is shown in Fig. 1. The chief difficulty with it was that the anode was necessarily small, which caused considerable anode slime, and sometimes this escaped to the cathode when the voltameter was being dismantled.

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[6] This Bulletin, 9, p. 157 (Reprint No. 194).

The other voltameter was Mr. Smith's new form, which possesses many advantages for work of high precision. This form has been described by him[7] as follows: "The voltameter has an anode in the form of a silver disk coated with electrolytic silver. This disk is contained in a shallow glass basin (with ground edge) supported by a glass rod passing through the center of the disk. A glass cylinder with ground ends fits over the basin and is used to separate the electrolyte into two parts, before and after the electrolysis." Fig. 2 shows a diagram of the voltameter, and Fig. 3 a photograph of it. With the lapse of time the significance of the

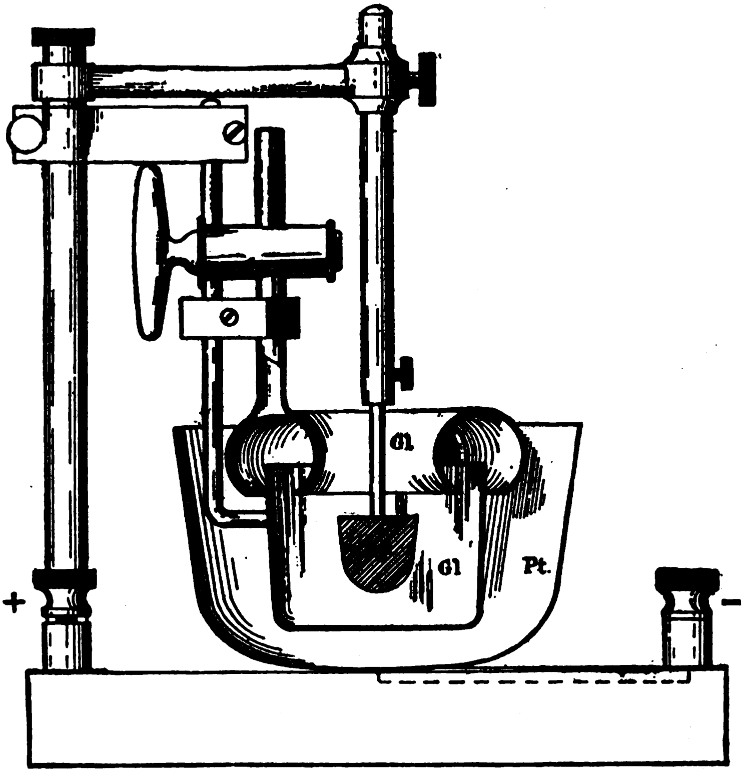

Fig. 1.—*Modified syphon voltameter*

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[7] The Nat. Phys. Lab. report for 1910, p. 32.

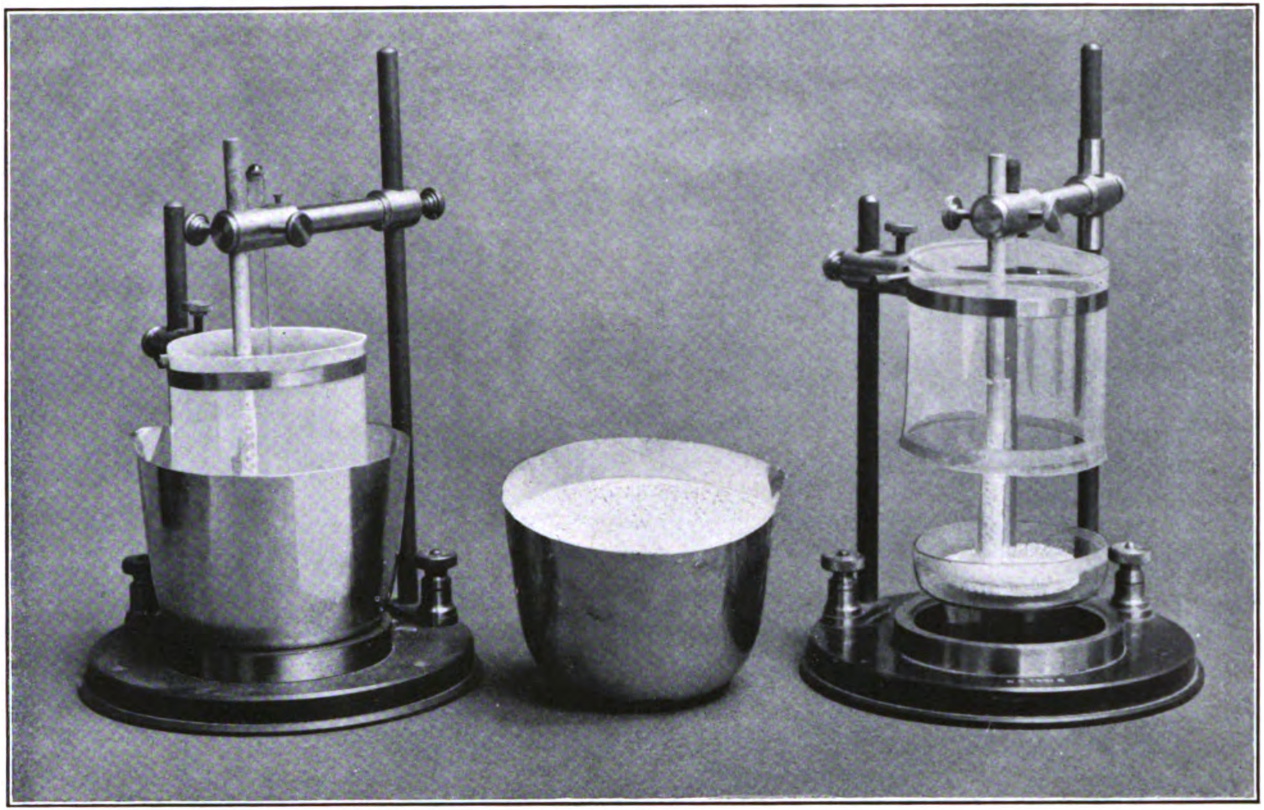

Fig. 3.—*Smith form voltameter*

name "new form," by which it was designated in the report of the International Committee, will vanish, and therefore we think it should be called the "Smith form" after the analogy of the Rayleigh and Richards forms.

The materials for the electrolyte used in these final experiments were of the best and satisfied the criteria that we have specified for a sufficient degree of purity. In some few cases we have employed electrolytes to which we have purposely added impurities of various kinds for the sake of experiment. We have endeavored to conduct this final series according to the best procedure learned from our previous work.

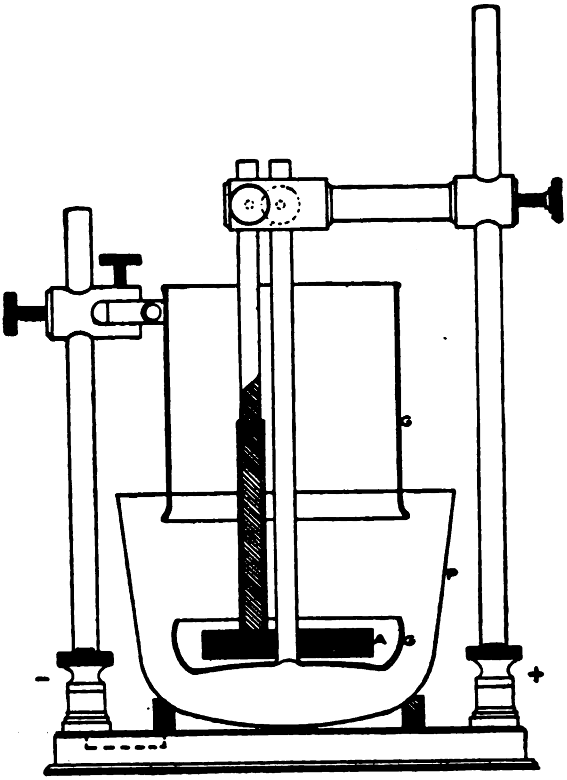

Fig. 2.—*Smith form voltameter*

D. TABLES OF RESULTS

The experiments naturally fall into three groups, of which the first began at the close of the International Technical Committee's work and continued until September 1, 1910. The second group occupied the months of October and November, 1910, during which time the quantitative measurements were made by Mr. G. E. Post, of this Bureau, in the absence of Mr. Vinal. The last series of measurements was begun in June, 1911, and continued until March, 1912. In taking the mean values for the various forms and sizes of voltameters these three groups have been separated in Table 8, so that the results at different periods of the work may be compared.

1. CORRECTIONS FOR ACID PRESENT

We have made considerable study of the effect of small quantities of acid in the electrolyte, and our results show that when acid is present in pure electrolyte the effect is to decrease the mass of the deposit. In a number of cases we have made comparative runs, using neutral electrolyte in one voltameter, and the same electrolyte made acid to a known amount in an exactly similar voltameter. After thus obtaining a number of values to express the decrease in the deposit for a given quantity of acid present, we have plotted them and drawn the curve shown in Fig. 4. Each point represents the difference in deposit of an acid voltameter from an exactly similar neutral voltameter. Both the porus pot and Smith's form of voltameters were used in this work, and the values obtained from the latter are indicated by solid dots. The two dotted curves represent the limits of $\frac{5}{100\ 000}$ either side of the mean experimental curve. They show that most of the determinations fall within these limits so that the general shape of the mean curve is fairly well determined, at least for acidities up to about 80 parts in 1 000 000 (0.008 per cent).

Examining the curve as it stands we find that for acidities below 10 parts in 1 000 000 equivalents of HNO_3, the correction (in parts per million) to be applied to the computed value for the cell to correct for the acid present, is sufficiently well given by the formula

$$y = -\ 4.5\ x.$$

For acidities ranging from 10 to 100 parts in 1 000 000 the following formula represents our results:

$$y = -4.5\ x + 0.02\ x^2$$

Beyond this point the experimental results are not sufficiently numerous or concordant to determine the form of the curve.

In Table 1 the values are given upon which this curve for the acid corrections is based. All determinations in which the electrolyte was believed to be pure are included, but the last two points are not shown on the curve. In a few instances acid tests were made on impure electrolytes and the scattering results will be discussed when the general question of acid is dealt with.

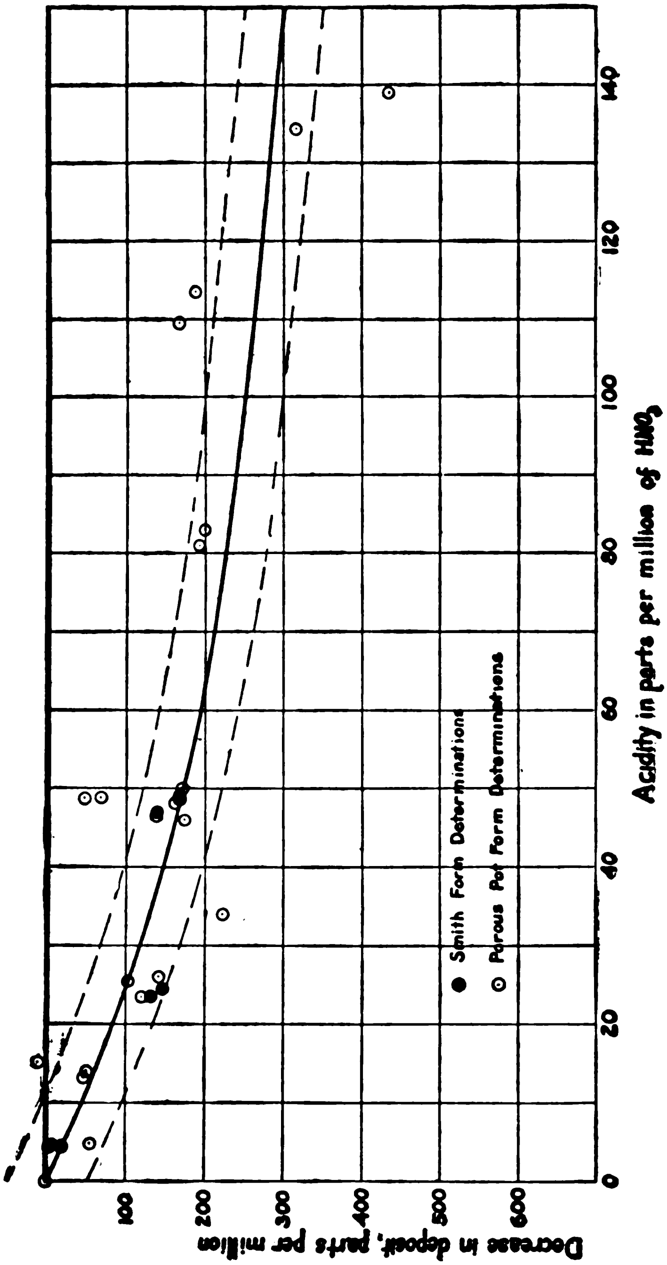

Fig. 4.—*Curve showing effect of acid on deposit*

TABLE 1

Relation of Decrease in Deposit to Amount of Acid in Electrolyte

[Pure electrolytes only]

Date	Form	Initial acidity	Final cathode acidity	Mean cathode acidity	Decrease in deposit	Remarks
		×10⁻⁶	×10⁻⁶	×10⁻⁶	pts. in 100 000	
Feb. 20, 1912	NF	4.7	4.1	4.4	0.2	Large.
Do.	NF	4.7	4.0	4.3	2.0	Small.
Do.	PP	4.7	4.8	4.7	0.6	Large.
Do.	PP	4.7	5.1	4.9	5.5	Small.
July 29, 1910	PP	13.2	13.2	13.2	4.6	Large.
Do.	PP	13.2	14.7	14.0	5.0	Medium.
Do.	PP	13.2	17.1	15.1	−1.2	Small.
Aug. 4, 1911	NF	24.0	23.0	23.5	13.1	Large - size; anolyte and catholyte mixed.
Do.	PP	24.0	23.0	23.5	12.0	Small.
Do.	PP	28. (?)	24.0	26.0	14.2	Medium.
July 28, 1911	NF	24.0	25.0	24.5	14.7	Large - size; anolyte and catholyte mixed.
Do.	PP	24.0	27.0	25.5	10.3	Small.
Do.	PP	Lost.	34.0	....	22.3	Medium.
Aug. 24, 1911	NF	48.0	46.0	47.0	14.0	Large.
Do.	PP	48.0	52.5	50.0	17.3	Gold cup; acid throughout.
Do.	PP	48.0	50.0	49.0	16.8	Small; acid throughout.
Do.	PP	48.0	44.0	46.0	17.5	Small; anode sol. neutral.
Do.	PP	48.0	45.0	46.5	14.0	Do.
Aug. 11, 1911	PP	48.5	49.0	48.7	16.9	Medium.
Do.	PP	48.5	48.0	48.2	16.3	Small.
Sept. 28, 1910	PP	51.6	46.2	48.9	6.7	Do.
Do.	PP	51.6	45.6	48.6	4.7	Do.
Aug. 11, 1911	PP	80.0	87.0	83.0	20.0	Small; gold cup.
Do.	PP	80.0	82.0	81.0	19.3	Small.
Do.	PP	115.0	106.0	109.5	16.7	Do.
Do.	PP	115.0	112.0	113.5	18.9	Do.
Sept. 7, 1911	NF	147.0	141.4	144.2	21.9	Large.
Do.	PP	147.0	121.7	134.4	31.6	Small; catholyte acid; anolyte neutral.
Do.	PP	147.0	132.2	139.0	43.5	Small; gold cup; catholyte acid; anolyte neutral.
Do.	PP	202.0	180.0	191.0	39.2	Small; catholyte acid; anolyte neutral.
Do.	PP	202.0	183.0	192.5	57.6	Small; gold cup; catholyte acid; anolyte neutral.

Dr. von Steinwehr in a recent article[8] denies that acid present in the electrolyte produces any effect on the deposit and quotes the following figures taken from the International Technical Committee's report to prove his contention:

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[8] Zs. f. Instr., **33**, p. 321; 1913.

Added acid	Deviation from normal value
5×10^{-6}	-5×10^{-5}
10×10^{-6}	-8×10^{-5}
100×10^{-6}	-12×10^{-5}
100×10^{-6}	-6×10^{-5}

If his theory were right, we should expect to find that in some cases the deposit was increased by the acid, which is not the case. It is very obvious from the above figures that acid decreases the deposit. We do not think the above data sufficient to calculate the relation between acid and decrease in deposit, and therefore have given in this paper much additional data on the subject. We will merely note here that if the above observations were plotted on the curve, Fig. 4, which we give, the first two would fall nicely on our curve. The fact that in all the cases where acid has been added to pure electrolyte 34 out of 35 cases showed a resulting decrease in deposit leaves no room for doubt that acid does decrease the deposit. Whether the law that we have derived from our observations is verified by future observers remains to be seen.

2. RESULTS OF THE POROUS POT AND SMITH NEW-FORM VOLTAMETERS

Having established the correction to be applied to the results in general for the presence of acid, we have tabulated the results obtained from the pure electrolytes having an acidity of 10 parts in 1 000 000 or less and applied to each the correction computed from the equation $y = 4.5\ x$ where y represents the change in deposit and x the mean cathode acidity, both being in parts per million.

Table 2 contains all the results with the porous-pot type of voltameter, arranged according to size of instrument. A few of the values are widely divergent from the mean, some being high and others low, but we have included all where the electrolyte conformed to our criteria of purity and no accident occurred.

Table 3, arranged similarly to Table 2, contains the results derived from Smith's form of voltameter.

In a few cases in each table the acid data are lacking or not sufficiently exact to warrant making the correction.

The total number of determinations with the Smith form was 55, from which we derive the arithmetical mean 1.01827_4, on the assumption that the variations in results between different sizes and at different times are accidental, and therefore each observation should have the same weight. Similarly, for the porous cup (156 observations) the arithmetical mean is 1.01826_7. The probable errors have been computed for a single observation and for the arithmetical mean, but the slight difference in favor of the porous-cup form we do not consider as proof of its superiority over the new form, but rather attribute it to our greater experience in using the porous-cup voltameter. This is substantiated by the fact that for the last series of observations with the large Smith form the probable error of a single observation is smaller. The slight difference in the mean results given by the two forms is just equal to the sum of the probable errors of the mean values. We give our final result as the mean of the arithmetical means with equal weight. Hence, after dropping the last figure we have as the voltage of the Weston normal cell at 20°

1.01827 VOLTS

Tables 4 and 5 give the results of the absolute determinations with the porous cup and Smith's form of voltameter for the cases in which the acidity of the electrolyte exceeded 10 parts in 1 000 000. Suitable corrections have been applied to each observation according to the formulas given on page 482. The means agree very well with the values given as the best results in the two preceding tables.

TABLE 2

Results with the Porous-Pot Form

[156 deposits. "Used electrolyte" designates that used previously]

Date	Large size				Medium size				Small size			
	Obs. value	Mean acidity	Correction	Cor. value	Obs. value	Mean acidity	Correction	Cor. value	Obs. value	Mean acidity	Correction	Cor. value
1910												
May 26[9]	1.01823	0.7	0_2	1.01823_2					1.01818_5	2.0	0_9	1.01819_4
26[10]	30	0.3	0_1	30_1					24	2.0	0_9	24_9
31									26_5	2.4	1_1	27_6
									25_8	2.2	1_0	26_8
June 3	25_4	0.1	0_0	25_4					26_0	1.3	0_5	26_5
7	31_0	3.8	1_7	32_7					24_3	1.6	0_7	25_0
									27_7	6.4	2_9	30_6
									27_6	6.5	2_9	30_5
10	34_8	5.5	2_6	37_4					31_0	6.4	2_9	33_9
									30_0	6.6	3_0	33_0
14	31_7	6.7	3_0	34_7					27_4	6.5	2_9	30_3
									26_6	6.9	3_1	29_7
17	37_1	1.8	0_8	37_9					34_7	2.2	1_0	35_7
									31_5	2.8	1_3	32_8
23	28_2	0.4	0_2	28_4					29_1	1.1	0_5	29_6
									26_8	1.0	0_4	27_2
27	24_1	0.3	0_1	24_2					28_4	0.9	0_4	28_8
									27_5	1.0	0_4	27_9
30	25_7	0.3	0_1	25_8					27_8	0.9	0_4	28_2
	26_9	0.4	0_2	27_1					27_6	1.2	0_5	28_1
July 5	22_4	0.4	0_2	22_6	1.01827_5	0.2	0_1	1.01827_6	26_7	1.5	0_7	27_4
	25_9	1.5	0_7	26_6	25_7	0.4	0_2	25_9	26_4	1.2	0_5	26_9
8					24_2	0.5	0_2	24_4				
					25_5	0.5	0_2	25_7				
12					25_9	0.5	0_2	26_1				
					27_8	0.5	0_2	28_0				
15	23_1	0.1	0_0	23_1	23_5	0.3	0_1	23_6	23_7	0.6	0_3	24_0
21	25_1	0.5	0_2	25_3	26_9	0.5	0_2	27_1	26_7	0.5	0_2	26_9
29	27_8	1.0	0_4	28_2	25_5	0.9	0_4	25_9	20_3	1.5	0_7	21_0
Aug. 2	25_7	1.0	0_4	26_1					23_1	1.1	0_5	23_6
2[11]									23_9	1.2	0_5	24_4
10					19_0	2.5	1_1	20_1				
					19_1	2.7	1_2	20_3				
18									25_7	1.7	0_8	26_5
									27_2	1.3	0_6	27_8
									26_1	1.3	0_6	26_7
									28_4	0.9	0_4	28_8
25	23_3	1.5	0_7	24_0	17_5	1.2	0_5	18_0	26_7	1.8	0_8	27_5
	29_9	2.0	0_9	30_8	19_6	1.9	0_8	20_4	39_1			
	23_0	2.2	1_0	24_0	25_4	2.7	1_2	26_6	30_5	1.1	0_5	31_0

[9] Used electrolyte.

[10] New electrolyte.

[11] Used electrolyte.

TABLE 2—Continued

Results with the Porous-Pot Form—Continued

Date	Large size				Medium size				Small size			
	Obs. value	Mean acidity	Correction	Cor. value	Obs. value	Mean acidity	Correction	Cor. value	Obs. value	Mean acidity	Correction	Cor. value
1910												
Sept. 1	16_9	......	0_0	16_9	15_6	......	0_0	15_6	15_4	......	0_0	15_4
	......	......	......	......	......	......	......	......	16_1	......	0_0	16_1
	......	......	......	......	......	......	......	......	16_9	......	0_0	16_9
28	26_4	0.1	0_0	26_4	......	......	......	......	22_0	0.3	0_1	22_1
	26_8	0.1	0_0	26_8	......	......	......	......	23_8	0.3	0_1	23_9
Oct. 11	22_4	1.0	0_4	22_8	19_2	1.1	0_5	19_7	29_1	1.4	0_6	29_7
	27_0	0.7	0_3	27_3	......	......	......	......	28_7	1.2	0_5	29_2
	......	......	......	......	......	......	......	......	22_2	1.1	0_5	22_7
	......	......	......	......	......	......	......	......	22_9	1.9	0_9	23_8
21	27_4	0.0	0_0	27_4	26_8	0.3	0_1	26_9	21_9	0.0	0_0	21_9
	23_2	0.3	0_1	23_3	26_2	0.4	0_2	26_4	19_2	1.0	0_4	19_6
29	[12] 27_4	1.2	0_5	27_9	......	......	......	......	29_0	......	0_0	29_0
	40_1	2.7	1_2	41_3	......	......	......	......	28_4	2.6	1_2	29_6
	......	......	......	......	......	......	......	......	29_3	......	0_0	29_3
Nov. 5	26_4	0.5	0_2	26_6	......	......	......	......	28_5	1.0	0_4	28_9
5	32_8	0.9	0_4	33_2	......	......	......	......	31_7	1.0	0_4	32_1
5	......	......	......	......	......	......	......	......	25_6	1.2	0_5	26_1
5[13]	......	......	......	......	......	......	......	......	27_0	1.2	0_5	27_5
15	20_6	1.3	0_6	21_2	......	......	......	......	25_3	1.9	0_9	26_2
	......	......	......	......	......	......	......	......	26_8	2.1	1_0	27_8
1911												
June 14	27_2	2.0	0_9	28_1	......	......	......	......	23_5	2.7	1_3	24_8
17	22_4	0.5	0_3	22_7	......	......	......	......	20_3	0.7	0_3	20_6
	......	......	......	......	......	......	......	......	22_0	0.7	0_3	22_3
23	26_8	0.3	0_1	26_9	......	......	......	......	26_9	0.6	0_3	27_2
	......	......	......	......	......	......	......	......	26_4	......	0_0	26_4
28	26_9	......	0_0	26_9	......	......	......	......	26_8	0.8	0_4	27_2
	......	......	......	......	......	......	......	......	27_8	0.7	0_3	28_1
July 6	25_6	0.5	0_2	25_8	......	......	......	......	26_6	1.0	0_4	27_0
	......	......	......	......	......	......	......	......	25_4	0.9	0_4	25_8
11	22_9	0.6	0_3	23_2	......	......	......	......	29_4	0.9	0_4	29_8
	......	......	......	......	......	......	......	......	29_2	1.0	0_4	29_6
17	25_6	0.6	0_3	25_9	......	......	......	......	27_7	1.6	0_7	28_4
28	......	......	......	......	29_8	1.3	0_6	30_4	24_4	1.3	0_6	25_0
Aug. 4	......	......	......	......	30_0	0.6	0_3	30_3	26_1	0.7	0_3	26_4
11	......	......	......	......	27_0	1.2	0_5	27_5	[14] [19_3]	......	0_0	......
24	......	......	......	......	......	......	......	......	22_5	0.3	0_1	22_6
	......	......	......	......	......	......	......	......	27_6	0.3	0_1	27_7
Sept. 7	......	......	......	......	......	......	......	......	31_7	1.9	0_9	32_6
	......	......	......	......	......	......	......	......	33_0	2.0	0_9	33_9

[12] Acidity for large one is final. [13] Used electrolyte. [14] Accident to bracketed observation.

TABLE 2—Continued

Results with the Porous-Pot Form—Continued

Date	Large size				Medium size				Small size			
	Obs. value	Mean acidity	Correction	Cor. value	Obs. value	Mean acidity	Correction	Cor. value	Obs. value	Mean acidity	Correction	Cor. value
1911												
Oct. 21									26_1		0_0	26_1
									28_3		0_0	28_3
26									22_9	3.8	1_7	24_6
									26_9	4.0	1_8	28_7
Nov. 9									29_1		0_0	29_1
									28_6	0.4	0_2	28_8
16	31_2	0.1	0_0	31_2	29_3		0_0	29_3	30_5	0.1	0_0	30_5
									29_0	1.1	0_5	29_5
22	32_6	0.0	0_0	32_6					27_7	0.4	0_2	27_9
Dec. 4	26_6	0.8	0_4	27_0					21_2	1.6	0_7	21_9
1912												
Jan. 16	26_7	2.0	0_9	27_6					28_4	1.9	0_9	29_3
Feb. 13	27_5	0.0	0_0	27_5					24_3	0.5	0_2	24_5
20	27_3	0.0	0_0	27_3					24_6	0.1	0_0	24_6
	26_7	4.7	2_1	28_8					19_1	4.9	2_2	21_3
Mar. 12	29_5	0.7	0_3	29_8					21_7	0.5	0_2	21_9
									25_8	0.4	0_2	26_0
Mean	1.01826_9		0_5	1.01827_4	1.01824_4		0_4	1.01824_8	1.01826_0		0_7	1.01826_7

Mean of all, 1.01826_7; average deviation, 3_0; probable error of single observation, 2_4; probable error of final result, 0_5.

TABLE 3

Results with Smith's Form.

[55 deposits]

Date	Large size				Medium size				Small size			
	Obs. value	Mean acidity	Correction	Cor. value	Obs. value	Mean acidity	Correction	Cor. value	Obs. value	Mean acidity	Correction	Cor. value
1910												
May 31	1.01820_8	0.2	0_1	1.01820_9	......	......	......	......	......	......	......	......
	25_2	0.2	0_1	25_3	......	......	......	......	......	......	......	......
June 3	23_6	0.0	0_0	23_6	1.01828_9	0.3	0_1	1.01829_0	......	......	......	......
7	23_4	3.8	1_7	25_1	18_5	4.0	1_8	20_3	......	......	......	......
10	22_9	4.8	2_2	25_1	20_4	5.1	2_3	22_7	......	......	......	......
14	20_9	6.2	2_8	23_7	16_7	5.9	2_7	19_4	......	......	......	......
17	22_2	1.5	0_7	22_9	18_3	1.7	0_8	19_1	......	......	......	......
23	32_6	0.3	0_1	32_7	35_8	0.1	0_0	35_8	......	......	......	......
27	24_8	0.2	0_1	24_9	......	......	......	......	......	......	......	......
Sept. 1	19_6	......	0_0	19_6	26_9	......	0_0	26_7	......	......	......	......
28	......	......	......	......	20_7	0.0	0_0	20_7	......	......	......	......
Oct. 11	26_9	0.9	0_4	27_3	29_1	0.9	0_4	29_5	......	......	......	......
29	23_2	......	0_0	23_2	......	......	......	......	......	......	......	......
Nov. 5	33_3	0.4	0_3	33_6	......	......	......	......	......	......	......	......
15[15]	25_1	1.5	0_7	25_8	......	......	......	......	......	......	......	......
1911												
June 14	30_6	2.0	0_9	31_5	40_4	......	0_0	40_4	......	......	......	......
17	35_2	0.5	0_2	35_4	37_4	0.5	0_2	37_6	......	......	......	......
23	30_6	0.3	0_1	30_7	29_4	0.3	0_1	29_5	......	......	......	......
28	24_2	......	0_0	24_2	28_3	......	0_0	28_3	......	......	......	......
July 6	27_6	0.5	0_2	27_8	29_6	0.4	0_2	29_8	......	......	......	......
11	22_9	0.3	0_1	23_0	25_2	0.2	0_1	25_3	......	......	......	......
28	25_0	0.8	0_4	25_4	......	......	......	......	......	......	......	......
Aug. 4	31_1	0.3	0_1	31_2	......	......	......	......	......	......	......	......
24	23_5	0.5	0_2	23_7	......	......	......	......	......	......	......	......
Sept. 7	33_0	1.3	0_6	33_6	......	......	......	......	......	......	......	......
Nov. 16[16]	28_6	0.0	0_0	28_6	28_8	......	0_0	28_8	......	......	......	......
22	......	......	......	......	29_4	......	0_0	29_4	......	......	......	......
1912												
Jan. 16	30_1	1.7	0_8	30_9	......	......	......	......	1.01831_1	1.7	0_8	1.01831_9
Feb. 13	28_7	0.0	0_0	28_7	33_3	0.0	0_0	33_3	......	......	......	......
20	28_8	......	0_0	28_8	......	......	......	......	29_7	......	0_0	29_7
	28_6	4.4	2_0	28_6	27_7	4.3	1_9	29_6	......	......	......	......
28	20_2	0.8	0_4	20_6	21_6	0.8	0_4	22_0	......	......	......	......
	21_6	0.8	0_4	22_0	......	......	......	......	......	......	......	......
Mar. 12	30_5	......	0_0	30_5	31_9	......	0_0	31_9	......	......	......	......
Mean	1.01826_3	......	0_5	1.01826_8	1.01827_6	......	0_5	1.01828_0	1.01830_4	......	0_4	1.01830_8

Mean of all, 1.01827_4; average deviation, 4_0; probable error of single observation, 3_4; probable error of final result, 0_5.

[15] Used electrolyte.

[16] 20 per cent electrolyte.

TABLE 4

Results with the Porous-Pot Form

HIGH ACIDITIES

Date	Large size				Medium size				Small size			
	Observed value	Mean acidity	Correction	Correct value	Observed value	Mean acidity	Correction	Correct value	Observed value	Mean acidity	Correction	Correct value
1910												
July 29..........	1.01823_2	13.2	5_9	1.01829_1	1.01820_5	13.9	6_0	1.01826_5	1.01821_6	15.0	6_6	1.01828_2
Sept. 28..........	....	......	......	....	....	......	......	....	16_1	48.9	17_4	33_5
									18_2	48.6	17_3	35_5
1911												
July 28..........	....	......	......	....	07_1	34	13_2	20_3	13_9	25.5	10_4	24_3
Aug. 4..........	....	......	......	....	15_8	26	10_6	26_4	13_9	23.5	9_8	23_7
11..........	....	......	......	....	09_8	48.7	17_3	27_1	10_5	48.2	17_2	27_7
									07_8	50.2	17_7	25_5
									07_3	49	17_4	24_7
									07_1	46	16_6	23_7
									10_6	46.5	16_8	27_4
Mean........	1.01823_2	......	5_9	1.01829_1	1.01813_3	......	11_8	1.01825_1	1.01812_7	......	14_7	1.01827_4

Mean of all 1.01826_5.

VERY HIGH ACIDITIES

Date	Observed value	Mean acidity	Correction	Correct value	Observed value	Mean acidity	Correction	Correct value	Observed value	Mean acidity	Correction	Correct value
1911												
Aug. 11..........	....	......	......	....	....	......	......	....	1.01806_6	83.5	23_7	1.01830_3
									07_3	81	23_4	30_7
									10_0	109.5	26_8	36_8
									07_8	113.5	27_7	35_5
Sept. 7..........	....	......	......	....	....	......	......	....	1.01787_9	139.8	29_5	17_4
									1.01800_1	134.5	29_0	29_1
									1.01791_3	192	33_6	24_9
									1.01773_5	193.7	33_7	07_2
Mean........	....	......	......	....	....	......	......	....	....	......	28_5	1.01826_5

TABLE 5

Results with the Smith Form

[High acidities in large size only]

Date	Observed value	Mean acidity	Correction	Correct value
July 28	1.01810_0	24.5	10_1	1.01820_1
Aug. 4	17_8	23.5	9_8	27_6
24	09_3	47	16_9	26_2
Sept. 7	10_7	144.4	29_9	40_6
Mean	1.01811_9	....	16_7	1.01828_6

3. RESULTS OF OTHER FORMS OF VOLTAMETERS

Table 6 contains the summary of results with the siphon voltameter, the modified siphon, and the Poggendorff forms. These results we do not regard as sufficiently accurate to include in the mean with the porous cup and Smith's form. The figures given for the siphon form are relative only, since it is not possible to maintain the current constant during the experiment, owing to the heating of the long column of electrolyte in the siphon. The modified siphon and the Poggendorff form present too great difficulties with the anode slime to be perfectly reliable. The mean of these 21 observations is 1.01832 volts, which although appearing much higher than the mean value found with the porous cup and Smith forms when using six figures is very near to the value adopted by the International Technical Committee (1.0183), as the voltage of the Weston normal cell at 20° C when we use five figures only. We now have five different forms of voltameter, giving results that fix the value to 1 in 10 000 quite certainly. We think that the reason these latter forms give higher values is the escape of anode slime to the cathode in the case of the modified siphon and Poggendorff forms. We are not clear why the siphon form generally gives results a little larger than the porous cup and Smith's forms.

TABLE 6

Results with other Forms of Voltameter

[Acidities small; no corrections made]

Date.	Siphon form[17]			Modified siphon	Poggendorff form
	Large	Medium	Small		
1910					
May 26	....	....	....	....	1.01829
	....	....	....	....	23
31	....	....	....	....	32_0
	....	....	....	....	24_8
June 3	....	....	....	....	26_4
17	....	....	....	....	40_8
23	....	....	....	....	31_4
27	....	....	....	1.01832_6	31_8
30	....	....	....	29_3	28_9
1911					
June 17	....	....	....	49_4	....
23	....	....	....	40_6	....
28	....	....	....	32_9	....
July 6	....	....	....	32_3	....
11	....	....	....	36_4	....
1912					
Jan. 22	1.01837_7	(1.01859_9)	1.01837_3	....	....
30	30_6	26_7	30_7	....	....
Mean	1.01834_1	1.01826_7	1.01833_6	1.01834_6	1.01829_7

Arithmetical mean: Siphon form, 1.01832_4; modified siphon form, 1.01834_6; Poggendorff form, 1.01829_7; mean (21 observations), 1.01832.

[17] Relative experiments.

4. MISCELLANEOUS RESULTS

Table 7 contains the results of the miscellaneous series of deposits in most of which the electrolyte was not pure and in some cases having been purposely contaminated for the sake of experiment. The several samples of salt as purchased could not be used for the higher precision work without further purification.

The salt from Poulenc, which was left with us by Prof. Laporte of the Laboratoire Central d'Électricité, was good in its original condition and was not improved by the simple means taken to purify it, while on the other hand, the Baird and Tatlock triple crystallized salt used July 17 was very bad in its original condition.

A single fusion, however, followed by a surface washing of the fused cake made it satisfactory, and it was repeatedly used in this way. The difference between the two salts is probably due to different impurities, although in the case of the Poulenc salt we did not have enough at our disposal to make the tests conclusive.

TABLE 7

Miscellaneous Deposits not Including the Experiments on the Effect of Acid

[The results recorded in this table are explained in the column of remarks. With a few exceptions, which are noted, they have not been included in the tables of best results]

Date	Large	Small	Remarks
1910			
July 8.....	1.01836_3	1.01827_6	Salt from Poulenc, recrystallized once and fused
	39_2	29_2	Salt from Poulenc, recrystallized once but not fused
12.....	1.01835_8	1.01824_9	Salt from Poulenc, fused but not recrystallized
	30_4	24_4	Salt from Poulenc, not fused and not recrystallized
Aug. 2.....	1.02095	1.02046	Filter paper extract added to electrolyte, neutral, very heavily striated
	074	040	Filter paper extract added to electrolyte, 10×10^{-6} acid very heavily striated
Aug. 10.....	1.01840_6	1.01829_3	Salt from Baker as purchased, $KMnO_4$ test not satisfactory
	39_1	27_4	Do.
18.....	....	1.01825_7	18 per cent pure electrolyte, included in mean of Table 2
		27_2	15 per cent pure electrolyte, included in mean of Table 2
		26_1	10 per cent pure electrolyte, included in mean of Table 2
		28_4	7 per cent pure electrolyte, included in mean of Table 2
22.....	8208.92	....	Milligrams, Septum a filter tube especially treated, electrolyte acid
	.50	....	Milligrams, Septum a filter tube especially treated, electrolyte neutral
Nov. 15.....	1.01829_6	1.01824_6	0.1 per cent of KNO_3 was added to the electrolyte
23.....	1.01852_1	1.01839_2	Baird and Tatlock electrolyte as purchased
		39_2	Do.
		35_6	Furfural, not polymerized, 5 in 10^{-5} parts added to electrolyte
		35_8	Do.
		1.02182	Deposit made in an atmosphere of CO_2
		88	Do.
1911			
July 17.....	1.01854_8	1.01845_0	Baird and Tatlock electrolyte as purchased, porous cup voltameter
	73_1	67_2	Baird and Tatlock electrolyte as purchased, Smith form
Oct. 21.....	....	1.01822_3	American made porous pot, coarse and thick
		19_6	Do.
		35_2	Pukal filter bulbs used as septum
		25_8	Do.
26.....	....	1.01821_9	American porous pots, same as on Oct. 21
		21_1	Do.
		38_8	Pukal filter bulbs, same as on Oct. 21
		36_1	Do.

TABLE 7—Continued

Miscellaneous Deposits not Including the Experiments on the Effect of Acid—Continued

Date	Large	Small	Remarks
1911			
Nov. 9.....	....	1.01825_9	American porous pots after especial efforts to put them in suitable condition
		27_6	Do.
		32_4	Pukal filter bulbs after especial efforts to put them in suitable condition
		32_8	Do.
27.....	....	1.01831_1	Piece of hard rubber suspended in the electrolyte, medium size
		32_1	20 per cent electrolyte with 2×10^{-6} alkali added
Dec. 4.....	1.01828_0	....	Piece of hard rubber suspended in the electrolyte
		1.01826_8	2×10^{-6} $Ba(OH)_2$ added to the electrolyte
		26_4	2.5×10^{-6} NaOH added to the electrolyte
14.....	1.01842_3	....	Smith form. The electrolyte was not completely freed from silica from long storage in glass bottles
	44_7	1.01839_6	Do.
		37_2	Porous cup. The electrolyte was not completely freed from silica from long storage in glass bottles
		30_1	Do.
1912			
Jan. 16.....	1.01836_7	1.01828_4	Second trial of the electrolyte of Dec. 14, porous-cup form
Feb. 28.....	1.01838_4	1.01826_6	Another electrolyte like Dec. 14 satisfying the $KMnO_4$ test but shows volume effect
		27_0	Do.
Mar. 1.....	1.01937_3	....	Electrolyte strongly contaminated with filter paper; deposit made for analysis

The deposits on August 18 are included in this table merely to draw attention to the fact that the variation in the concentration of the electrolyte is without any certain effect on the deposited silver. These deposits were perfectly normal and have been included in the results given in Table 2. The deposits made November 23 in an atmosphere of CO_2 show a great increase in the mass of deposit. They were strongly striated and so tightly adherent that it was impossible to loosen any of the silver with a glass rod.

Beginning on October 21 we made several experiments on porous pots other than the particular kind that we have adopted for this work. The kind which we have designated in the table as "American made" were purchased in 1907. They are slightly conical in shape and somewhat thicker and coarser than the kind we generally use. They have the added disadvantage of containing considerable quantities of iron. In the first two experiments some difficulty was experienced in getting the cups in proper condition, as the electrolyte at the end of each experiment was decidedly acid. In the third (Nov. 9), however, the conditions were better and the weight of deposit normal. The Pukal bulbs gave consistently high values, although they are made, presumably, of the same material as our best porous cups. The cause of this is not certainly known, but owing to the smallness of the anode that must be used, because of the narrow neck of the bulb, some trouble might perhaps be expected, and such bulbs should not be used. Our results are too few in number to settle the question definitely. The tests made with hard rubber in the electrolyte were for the purpose of showing whether or not the hard rubber friction rings which we have used to support the porous cups were likely to produce errors owing to the electrolyte creeping up the sides of the porous cups by capillary action and in this way wetting the rubber. Jaeger and Von Steinwehr have actually immersed the rubber in the electrolyte as a support for the porous cup. Our results show that this is probably permissible, though as a matter of precaution we think that such foreign substances should be kept out of the electrolyte as far as possible.

Two electrolytes are quoted as showing a volume effect although they satisfied the permanganate test. This may be due to the presence of some such colloid as silica from too long storage in glass containers (Part III, p. 543), which would not affect the $KMnO_4$ test but may increase the deposit. This case is the exception rather than the rule and does not invalidate the value of the $KMnO_4$ test, if proper precautions are taken when preserving the electrolyte in glass. We think, however, that the possibility of this case arising emphasizes the necessity of specifying the volume test also as one of the criteria for the purity of the electrolyte.

III. SPECIAL INVESTIGATIONS

A. ON THE AGREEMENT OF VARIOUS FORMS

1. COMPARATIVE RESULTS

At various times during the course of the work relatively large differences have appeared between the porous-cup form of voltameter and Smith's new form, but in general it has not been possible to find the cause of the difference, although numerous attempts have been made to do so. This is because the difference has usually almost vanished, the two forms drawing together as the investigation proceeded. The results given in Tables 2 and 3 show the average difference between the two forms to be only 7 in 1 000 000, which is sufficiently good agreement for a primary standard at the present time. Comparing the values of the present paper (3d series), taken in groups at different periods of the work, we find the agreement to be in general very good. The results are thus shown in Table 8. Table 9 shows the values obtained from these two forms at different periods, dating back to the beginning of the Bureau's investigation.

TABLE 8

Mean Values for Weston Cell at Different Periods of the Work

Date	Smith form						Porous-pot form					
	No.	Large	No.	Medium	No.	Small	No.	Large	No.	Medium	No.	Small
May 26 to Sept. 1, 1910	10	1.01824_4	7	1.01824_7	....	....	21	1.01827_3	15	1.01823_7	36	1.01826_9
Sept. 28 to Nov. 23, 1910	4	1.01827_6	2	1.01825_1	....	....	11	1.01827_7	3	1.01824_3	17	1.01826_4
June 14, 1911, to Mar. 12, 1912	18	1.01828_1	12	1.01830_5	2	1.01830_8	15	1.01827_4	4	1.01829_4	34	1.01826_7
Means according to size	32	1.01826_8	21	1.01828_0	2	1.01830_8	47	1.01827_4	22	1.01824_8	87	1.01826_7

Date	Mean according to form				Mean of both	
	No.	Smith	No.	Porous pot	No.	
May 26 to Sept. 1, 1910	17	1.01824_6	72	1.01826_3	89	1.01825_5
Sept. 28 to Nov. 23, 1910	6	1.01826_7	31	1.01826_7	37	1.01826_7
June 14, 1911, to Mar. 12, 1912	32	1.01829_1	53	1.01827_1	85	1.01828_1

TABLE 9

Comparison of Recent Values for the Weston Normal Cell

Date	Observations	Voltameter	Deposits	Value for cell
1908-9....	First series, Bureau of Standards..........	Porous cup..................	42	1.01828_7
1909-10...	Second series, Bureau of Standards.......	Small porous cup............	44	1.01827_5
1910......	International Technical Committee........	Porous cup..................	14	1.01828_6
1910......	.....do..................................	Smith's form................	8	1.01828_7
1910......	Smith and Vinal at Teddington............	Porous cup..................	15	1.01821_8
1910......	.....do..................................	Smith's form................	19	1.01830_4
1911-12...	Third series, Bureau of Standards........	Porous cup..................	156	1.01826_7
1911-12...	.....do..................................	Smith's form................	55	1.01827_4

Mean of 271 determinations, porous cup, 1.01827_0; mean of 82 determinations, Smith's form, 1.01828_2.

2. POSSIBLE EXPLANATIONS OF OBSERVED DIFFERENCES

Notwithstanding the fact that the difference between the final average values of the two forms of voltameters is only seven parts in 1 000 000 (Tables 2 and 3), there is reason for believing that this is not accidental, but on the contrary is due to causes that are persistent. We have given much study to the cause of this difference as well as to the differences between the different sizes of voltameters of each form, and present the following discussion of the possible causes of the small differences.

First. The data on acidity show that if neutral electrolyte is employed the acidity of the cathode electrolyte at the conclusion of the experiment is on the average higher by a few parts in a million in the porous-pot form than in the Smith form. This circumstance may account in part at least for the lower values obtained in the former type, since the effect of acid upon the deposit from a pure electrolyte is to decrease it slightly.

On the other hand, it is quite as certain that the very concentrated electrolyte formed around the anode in both forms of voltameters may become very slightly basic. In view of the fact that in three of the deposits made by the International Technical Committee (report, pp. 157-158) a few parts per million of added base caused a heavy striated deposit, it seems possible that this base formed around the anode may be another cause of the difference between the two forms. It is to be noted in this connection, however, that the basic anode electrolyte formed in the voltameter is not opalescent and therefore the silver hydroxide is probably not colloidal, so that its effect is doubtless not nearly so pronounced as in the case of the added base. Nevertheless, there is a possibility of the formation of colloidal hydroxide at the cathode if any of the anode solution reaches the layer of dilute electrolyte next the cathode; for it is known that silver hydroxide is much less soluble in dilute than in concentrated silver nitrate solution.

It is known also that colloidal silver hydroxide may remain undissolved in presence of more than its equivalent amount of nitric acid. Therefore the possibility that nitric acid may be found at the cathode equivalent in amount to the base formed at the anode does not vitally affect the question of the formation of colloidal silver hydroxide near the cathode.

Second. In the paper recently published by Washburn and Bates [18] they emphasize the reversibility of the iodine voltameter, and it was with a view to ascertaining the limits within which the silver voltameter might be said to be reversible that we undertook a series of measurements described in this paper under the head of "Reversibility." One fact was noted in these experiments which offers the second possible explanation of the differences between the porous cup and new form of voltameter and also why the small sizes of new form voltameter should give heavier deposits than the larger size.

The anodes in the experiment of March 11 were two large size bowls, one containing a pure crystalline deposit and the other strongly striated, each being about 10 grams. These bowls were connected to smaller bowls, serving as cathodes, by glass siphons. The electrolyte in both was made from pure salt. The current passed through them was one-half ampere for one hour, thus transferring about 2 grams of silver from the large bowls to the small ones. At the conclusion of the run the voltameters were carefully dismantled and both anode and cathode bowls carefully washed, dried, and weighed. The quantitative results are not of interest here, but only the fact that the conditions found in the two anode bowls were radically different. That which contained the pure silver deposit was white and contained relatively little anode slime. This too was white and fairly coarse so that it did not present any serious difficulty in the washing of the bowl. On the other hand, the cup containing the striated deposit was very dark in color and contained a very large quantity of slime which made much trouble in the washing. The only practical method of collecting this without filtering the requisite four or five liters of wash water through a small quantitative filter paper was found to be an hourly examination of the water in large beakers, collecting each time the sediment as it slowly settled to the bottom. After the first large amount had been collected and returned to the bowl, the wash water was apparently perfectly clear, but considerable quantities of fine brownish slime could be collected at each time that the liquid was examined.

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[18] J. Am. Chem. Soc., 34, p. 1341; 1912.

The bearing which this fact has upon the difference between the Smith form and the porous cup consists in emphasizing the necessity of using pure electrolyte in forming the anode for the former. In general no great pains have been taken as to the purity of the solution used in the preparation of the anodes, and past experience has shown that the amounts of slime seen on the anode in the Smith form varied considerably without any definite reason being known. It is easily conceivable that some of the invisible slime which took 24 hours to settle out of the wash waters may have exercised some influence in increasing the deposit in the new form over the porous-cup form, since in the latter it could not pass through the porous cup. This would also explain why the small Smith form gives larger deposits generally than the large size, since obviously the same amount of slime would probably be formed in the two sizes when run in series, the anodes being alike, and the effect would be proportionately greater in the smaller volume of solution. This also may explain why the difference between the two forms has varied somewhat at different times, since if this theory is correct the difference would depend to some extent at least on the electrolyte used for forming the anode. The hopeful fact remains, however, that there is little evidence of trouble with the Smith form if the anode is formed in pure electrolyte. It is of course possible to put this theory to a crucial test and such was planned, but the urgency of other work prevented more than one experiment being made. Hence we can not lay much emphasis on the result obtained, although it is in the right direction according to the theory.

Form	Anode	Deposit	Difference
New form, large.	Prepared from impure electrolyte	4231.87	3 parts in 100 000
	Prepared from pure electrolyte	4231.75	

Other observations on the effect of impure anodes are given under the head of "Reversibility of the voltameter," page 523.

B. ON THE ACCURACY OF THE MEASUREMENTS

We have given at the end of Tables 2 and 3 a statement of the probable error of a single measurement and also of the probable error of the arithmetical means. Since the probable error of the means is equal to the probable error of a single observation divided by the square root of the number of observations we may readily find by putting the probable error of the final result equal to some arbitrary figure, as, for example, 1 part in 100 000 that if the probable error of a single observation is 3.4 parts in 100 000 as in the case of the Smith form that the number of observations required is 12 and similarly for the porous pot 7 observations, which, however, must be independent in the sense that each result is the result of a different experiment and on the assumption that the accidental errors are of the same magnitude as in the present work. From the above it would appear that somewhat better agreement might be expected in the results recorded in Table 9 if the errors entering were purely accidental, which is certainly not the case. Perhaps the chief error arises from a variation in the electrolyte.

We know that the electrolyte used in the first two series of experiments was not as pure as in the last and therefore we have selected out the small size porous-cup voltameters as being the more accurate for reasons which we have given in connection with the volume effect. It is to be expected then that these results should be somewhat above the average. The most notable exceptions are the results obtained by Smith and Vinal at Teddington for which no satisfactory explanation has been found. For the last series the results are based on the determinations with what we believe to have been the purest salt and are probably the most trustworthy.

In making determinations in the future for checking the constancy of the Weston normal cell we believe that as many different samples as possible of $AgNO_3$, each conforming to the required standard of purity, should be used to avoid systematic errors.

One further possible source of error remains to be mentioned. We have been dependent on wire standards for our value of the ohm and we have endeavored to conform always to the same basis. It is, however, possible that a slight drift may have taken place during the years that have been consumed in this investigation. Similarly there is an uncertainty as to how nearly the cells measured represent the Weston normal cell. However, these uncertainties are probably less than one part in a hundred thousand, and for want of any knowledge as to their magnitude no correction can be applied.

C. RELIABILITY OF IODEOSINE AS AN INDICATOR

In the previous paper of this series (this Bulletin, **9**, p. 529) a method was described for the determination of small amounts of free acid or alkali with an accuracy of at least 1 part per 1 000 000. In order to obtain such a degree of accuracy it can be shown that an indicator must be selected, the turning point of which is below $[H^+] = 10^{-6}$, i. e., the indicator must be sufficiently sensitive to detect free nitric acid if the latter is hundred-thousandth normal (0.00001 N $HNO_3 = 0.63$ parts HNO_3 per 1 000 000). In order to determine whether iodeosine as used in the method described possesses this degree of sensibility, tests were made in which solutions of pure potassium chloride and nitrate were titrated after the addition of known small amounts of acid or alkali, using both iodeosine and methyl red as indicators. In every case the results with these two indicators agreed within 0.05 cc of 0.001 N acid, equivalent to about 0.3 part per 1 000 000 of nitric acid. In general it was found that methyl red was nearly as sensitive as iodeosine and for an accuracy of 1 part per 1 000 000 could be substituted for it in these titrations. In using methyl red as the indicator, about one drop of the indicator solution (0.2 per cent in alcohol) is added to 10 cc of the solution to be tested and the titration carried out directly in a small flask or beaker, the operation therefore being much more convenient than when iodeosine is used. The conclusion of Tizard[19] that methyl red changes at about 10^{-6} was confirmed by experiments with a hydrogen electrode, using solutions of potassium chloride, the reaction of which was changed by the addition of known amounts of 0.001 N acid or alkali. While such a method is not suitable for the very accurate preparation of solutions of known hydrogen ion concentration, it obviated possible effects of foreign salts, since the solution used with the hydrogen electrode was similar to that present in the titrations.

Since the iodeosine, under the conditions used, was found to be slightly more sensitive to acid than the methyl red, it follows that the iodeosine has effectively a turning point below $[H^+] = 10^{-6}$ and is therefore suitable for detecting as little as 1 part in 1 000 000 of free acid or alkali. As the exact turning point of the iodeosine is no doubt dependent upon the concentration of the iodeosine in the ether solution and aqueous phases, the above conclusion only applies with certainty to titrations carried out under approximately the conditions recommended in the method as described. For the comparisons of these indicators with the hydrogen electrode we are indebted to Dr. William Blum, of this Bureau.

D. EFFECT OF ACID

We have given above a discussion of the effect of acid in the electrolyte on the deposit of silver and have shown that when the electrolyte is pure the silver deposit is less than normal, depending on the amount of the acid present. We purposely limited the discussion at that point to the case of pure electrolytes, since we wished to derive a correction to be applied to the observations in our tables of best quantitative measurements where only pure salt was used.

1. EFFECT ON IMPURE SOLUTIONS

When acid is added to solutions that are impure the effect can not be predicted, since it depends on the nature of the impurity. The following experiments show a case where an electrolyte believed to be pure and yielding satisfactory results in the voltameter was made to show a pronounced volume effect by the addition of a small amount of pure nitric acid.*

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[19] J. Chem. Soc., 97, pp. 2477–2490, 1910.

TABLE 10

[Using porous-cup voltameters]

Date	Neutral electrolyte		Acid electrolyte		Size bowl
	Value	Mean acidity	Value	Mean acidity	
		pts. in 10^6		pts. in 10^6	
July 15, 1910	1.01823_1	0.1	1.01832_1	9.3	Large
	1.01823_6	0.3	1.01822_3	10.3	Medium
	1.01824_0	0.6	1.01818_8	9.9	Small
July 21, 1910	1.01825_3	0.5	1.01824_6	10.2	Large
	1.01827_1	0.5	1.01820_0	9.9	Medium
	1.01826_9	0.5	1.01819_4	9.9	Small

On the other hand, the experiment of August 2 showed that the addition of acid to electrolyte containing considerable filter paper extract might produce the opposite effect. Using two large and two small porous-cup voltameters with enough filter paper extract added to the electrolyte to produce a very high value for the cell we found the following results:

Size	Neutral electrolyte	Acid electrolyte
Large	1.02095	1.02074
Small	1.02046	1.02040

The terms acid and neutral electrolyte used in connection with so contaminated a solution are merely relative, since the acidity of the solution changes so fast when thus contaminated that exact measurements are not possible. (See p. 247, Pt. II, of this series of papers, this Bulletin, vol. 9.) The acid added in this experiment would have been sufficient to render a pure solution acid by 10×10^{-6} parts.

Continuing this line of work, we next tried a very resistant cellulose. In this experiment two filter tubes that had been washed with hot distilled water to dissolve the soluble celluloses were used in two large Rayleigh voltameters. They were assembled the night before the experiment with the purest electrolyte, and nitric acid to make the electrolyte 30×10^{-6} parts acid was added to one. At the conclusion of the experiment there was only 15×10^{-6} parts acid found in this voltameter. The resulting deposits were as follows: From neutral electrolyte, 8208.50 mg; from acid electrolyte, 8208.92 mg.

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* The presence of an impurity in this silver nitrate was later confirmed by the permanganate test.

The result would seem to show that the acid broke up the resistant cellulose into reducing agents and thereby caused heavier deposits.

It is quite apparent from these experiments that the effect of acid in impure solutions is uncertain and we think that enough has been said to indicate that acid may sometimes increase the deposit, as in the experiment of July 15. Smith[20] concludes that the effect of nitric acid is to lower the deposit but notes that the effects are very irregular, in some cases a marked increase resulting. We think that the phenomena he observed are explained by the variations in the purity of the electrolyte.

2. NATURE OF THE ACTION OF ACID

To explain why the acid lowers the deposit when added to pure electrolyte is very difficult and in spite of numerous qualitative experiments no certain explanation has as yet been found. Leduc[21] has given much attention to this question; he, however, thinks that when acid is formed in the voltameter it originates at the anode, but this seems doubtful from our experiments as we shall show later. It is of course possible that the hydrogen migrating to the cathode may take part in secondary reactions, but the experimental difficulties in obtaining definite data as to what these may be are very great. We have tried experiments of letting acid in water solutions of known strength stand on silver deposits without the passage of electric current and have estimated the silver dissolved by careful titrations with ammomium thiocyanate. The amounts found, however, were very small even for acid of normal strength standing over night and the results showed the surface condition of the silver to be the important thing rather than the amount of acid or the length of time of contact. No conclusion can therefore be drawn as to whether there is a possible corrosion of the cathode deposit or not.

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[20] Phil. Trans. A **207**, p. 594; 1908.

[21] J. de Physique I, p. 561; 1902.

In another direction, however, we could fortunately get definite and satisfactory results.

It seemed possible that in the case of an electrolyte which was appreciably acid the decrease in the silver deposit might be due to a depositing out of the hydrogen ions before the silver begins to deposit since there is probably at the instant the current begins to flow a greater difference of potential at the cathode than obtains afterwards, as the discontinuous character of the deposit indicates that the potential difference must break through a sort of surface film and establish outlets[22] for the current to the platinum cathode. If this were possible, by making deposits of about 1 milligram each from solutions containing acid and without the difference ought to be quite apparent.

The deposits were all made in large size bowls with the acidity of the electrolyte carefully determined. The time of the deposit and the current used were varied, but always made to yield about 1 milligram of silver theoretically. The time was measured by a chronograph, except for the longest run, and the current by a milammeter. Following this the deposits were carefully washed. To determine the amounts of silver deposited several methods were tried since the weighing of so small a deposit was unduly laborious. Experiments with the nephelometer showed that the precipitate of silver chloride formed after the deposits had been dissolved out of the cups with nitric acid were too heavy to use this instrument with satisfaction. In the end it was found best to use a $\frac{N}{1000}$ solution of ammonium thiocyanate with ferric ammonium alum as the indicator after the titrating solution had been standardized with a standard silver solution. By this means very satisfactory results were obtained. The silver deposits were removed from the bowls by hot HNO_3 and water 1:3.

The results are given in the following table, together with the results of several similar experiments in which the cups were first electrolyzed for four hours to fill them with oxygen or hydrogen. In this case there appears to be a decrease in the deposit in the oxygenated cup that did not appear again after the first time it was used. The effect of oxygen in the cup thus appears to be smaller than has been previously supposed. The slight gain in the hydrogenated cup is not readily explainable. The titrations are estimated to be good to about 0.05 milligram of silver. The result of these experiments is to show pretty certainly that the presence of acid does not cause the diminution of the deposit by a preliminary deposition of hydrogen before the silver begins to deposit. Except for eliminating this possible explanation, however, it throws no light on the mechanism of the effect of acid.

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[22] See The Silver Voltameter, Part II, this Bulletin, 9, p. 278 (Reprint 195).

TABLE 11

Experiments to Determine the Initial Effect of Acid, and Oxygen and Hydrogen

Date	Cup	Acidity of electrolyte	Current	Time	Calculated deposit	Observed deposit	Remarks
1912			amps	sec	mg	mg	
Dec. 14	93	11×10^{-6} acid............	.040	25.0	1.118	1.13	Deposit almost invisible
	95	Neutral..................	.040	25.0	1.118	1.13	Do.
15	93	11×10^{-6} acid............	.0000069	147060.	1.13	1.10	Deposit consisted of 13 crystals in each cup
	95	Neutral..................	.0000069	147060.	1.13	1.10	
16	93	11×10^{-6} acid............	.189	6.94	1.465	1.42	
	95	Neutral..................	.189	6.94	1.465	1.42	
18	93	211×10^{-6} acid............	.207	5.20	1.204	1.24	
	95	Neutral..................	.207	5.20	1.204	1.16	
18	93	211×10^{-6} acid............	.050	19.81	1.107	1.15	
	95	Neutral..................	.050	19.81	1.107	1.10	
19	95	.....do....................	.040	24.80	1.11	1.33	Cup hydrogenated for 4 hours
	93	.....do....................	.040	24.80	1.11	0.91	Cup oxygenated for 4 hours
19	95	.....do....................	.040	24.81	1.11	1.02	Immediately following the preceding. No further treatment of the cups
	93	.....do....................	.040	24.81	1.11	1.03	
20	95	.....do....................	.040	24.89	1.113	1.20	Cup hydrogenated for 4 hours
	93	.....do....................	.040	24.89	1.113	0.93	Cup oxygenated for 4 hours
20	95	.....do....................	.040	24.55	1.098	1.05	Immediately following the preceding. No further treatment of the cups
	93	.....do....................	.040	24.55	1.098	1.03	

E. INFLUENCE OF SEPTA OTHER THAN FILTER PAPER

1. SILK

The influence of silk upon the weight of silver deposit has been discussed in the first paper. The explanation of this effect will be briefly considered here.

Ordinary raw-silk cloth purchased in the open market, part of which has been used as septa in voltameter work, was extracted with pure neutral double distilled water. The extract was distinctly basic toward iodeosine (in ether-water solution). The extract from approximately five grams of the silk was distilled and the distillate tested for furfuraldehyde by means of the very sensitive xylidine test described in the second paper of this series. No reaction for this aldehyde was obtained. However, the distillate restored the color to magenta solution which had been decolorized with sulphurous acid, thus indicating the presence of an aldehyde of some kind. No attempt was made to identify the particular aldehyde (or aldehydes) formed.

Examination of these aqueous extracts of silk (after careful filtration through asbestos and finely divided platinum) by means of the ultra microscope, showed them to be distinctly colloidal in character.

It is thus apparent that the chemical and physical properties of aqueous extracts of raw silk (unwashed) are very similar in these important respects to the aqueous extracts of filter paper except as to the particular kind of aldehyde formed by its decomposition, so that their very similar influence in the voltameter is probably due to the same causes, viz, the production of permanent colloidal solutions of metallic silver. Indeed such silver hydrosols have been formed and they are very similar in appearance to those prepared from filter paper.[23]

The effect of thoroughly washed silk, or more especially of silk which has been used repeatedly in the voltameter is somewhat different. In this case the silk is not decomposed into aldehydes (which probably come from the so-called silk glue) but may be hydrolysed, perhaps, into amino acids thus rendering the electrolyte acid and in consequence decreasing the weight of the silver deposit. Some experiments on this decomposition are given in International Report, page 179.

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[23] The influence of gelatine is probably due to the same cause.

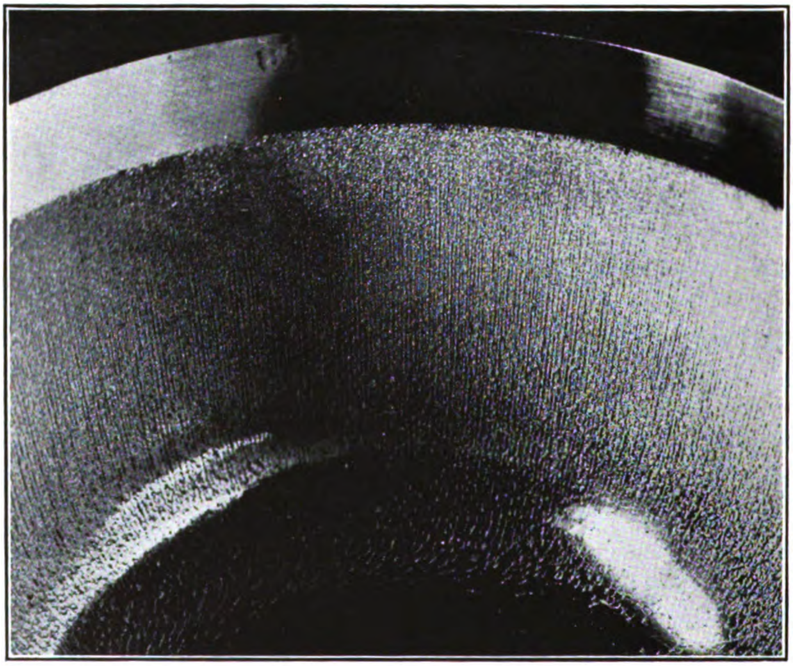

Fig. 5.—*Showing striations due to silk*

The above discussion of the action of silk on the electrolyte was written before we read Von Steinwehr's recent article,[24] in which he denies this effect. We have stated that the initial effect of silk in the voltameter is analogous to filter paper and have presented chemical evidence to prove it. To supplement this we publish here a photograph (Fig. 5) of a striated deposit (made while the International Committee was working in Washington) resulting from the use of pure raw silk.

This is a photograph of deposit No. 69 in the tenth experiment made by the International Committee May 2, 1910. The pure raw silk used had been thoroughly washed, but had been kept dry for about two months and was washed again just before the experiment. The value for the cell computed from this deposit was 1.01855, which is abnormally high, being 28 in 100 000, above the mean value. A piece of the same silk was wrapped around a porous cup in deposit No. 71 of the same experiment and increased the deposit over its mate No. 70 by 32 parts in 100 000. This seems to us conclusive evidence that silk is a dangerous substance to use in the voltameter.

As to the second effect of silk, whereby acid is produced, we wish to clearly state that this effect does not influence the result simultaneously with the effect mentioned above. It appears only after the prolonged use of the silk has removed the soluble so-called "silk glue," which gives rise to the effects analogous to filter paper. Table LV of the International Report shows that two samples of silk used by the German delegate produced on the average 30×10^{-6} parts of acid in 160 cc of electrolyte after shaking all together for 24 hours. We tabulate below all the silk observations made by the German delegate in the experiments conducted by the committee as a whole. We give the absolute value computed for the cell in each case except the last where it is not available. In this case we have assigned the value 1.0183 adopted by the committee to the mean deposits obtained by the English, French, and American delegates and on this basis have computed values for the German cups. In column Δ we give the differences between the mean values and the 1.0183 value adopted by the committee.

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[24] Zs. f. Instr., 33, p. 321; 1913.

TABLE 12

Showing Effect of Silk on Voltameter Deposits

Date	Value	Mean	Δ
1910			$\times 10^{-5}$
Apr. 15	1.01830_4	1.01830_4	$+ 0_4$
20	827_5		
	837_8	832_6	$+ 2_6$
26	823_6		
	820_9	822_2	$- 7_8$
May 2[a]	....	....	....
7	824_6	824_6	$- 5_4$
14	1.01806		
	1.01773	1.01789	-41_6

[a] Mixed loose silver from filter paper and silk voltameters so that value for silk is not available.

It will be observed that the concordance of the results given by the German delegate with the results obtained by the other delegates as shown by his Tables LVI, LVII, and LVIII in the Report to the International Committee is due partly to the values obtained with voltameters which had no silk. They did not include the observations of May 14 since no absolute values could be computed for these.

Examining the table we have given above we see that his silk voltameters were in agreement with the adopted value at the start or even slightly above, but that the values decreased until at the end most abnormally low values were found.

In spite of all this Von Steinwehr calls the Kohlrausch form of voltameter one free from all trouble and with the highest claim to be a satisfactory instrument.

2. POROUS POTS

We began to make observations on the possible effects of the porous pot upon silver nitrate as early as September, 1909. These tests included the question of the solubility of the materials of the pot in water, the methods of removing from the pores the acid and other chemicals used in cleaning the pots, the cause of the darkening of the pots after long use, their effectiveness as filters, and several other minor questions. As a result of these tests we adopted a standard method for cleaning and preparing the pots for use in the voltameter, and this method was described in an earlier paper of this series. Unless otherwise stated, all the pots were those made by the Königlich Porzellan Manufaktur. The results of these investigations (made between September, 1909, and February, 1910), on which this method of treatment was based, may be summarized as follows:

The best "conductivity water" (specific conductivity 1×10^{-6}) dissolves a very slight amount of electrolytes from new unused and untreated porous pots when the water is allowed to slowly filter through the pores, the first few cc of such a filtrate showing a specific conductivity varying from 2 or 3×10^{-6} to about 10×10^{-6} or even greater. Such filtrates also show a basicity toward iodeosine varying from 2 or 3 parts in 1 000 000 to a few parts in a hundred thousand (in terms of NaOH).

Repeated washing of new unused pots reduces this "solubility" of the pot to a point where the change in the specific conductivity of pure water produced by filtering the water through the pores is less than 1×10^{-6}, but this requires a great number of washings and is not a practical method of rendering the pots insoluble.

The pots are most easily rendered insoluble (as shown by conductivity measurements and neutrality tests with iodeosine upon the water filtrates) by filtering dilute nitric acid through them and subsequently washing out the acid by filtering successive portions of twice distilled water through them until neither the conductivity nor the neutrality of the water is appreciably affected by the filtration; that is, the specific conductivity of the water must not be changed by more than 1×10^{-6} and the basicity (or acidity) by more than 1 part in 10^6 (in terms of HNO_3). The pots can easily be gotten into this very insoluble condition by one treatment with acid and four or five washings with water. When the pots are heated to redness or above in an electric oven (to remove silver stains or other impurities from the surface and from the pores) they are much more alkaline (after cooling), i. e., the first portions of water filtered through them are strongly alkaline. This is due to the partial volatilization of the combined alkalis of the silicates of which the pots are composed, the free alkali condensing in the pores and on the surface as the pot cools. This free alkali may be quite easily removed by allowing one or two portions of dilute nitric acid to filter through. When this acid is removed with the water as before, the pot is again in a highly insoluble condition.

When a 10 per cent solution of pure silver nitrate is filtered through a clean porous pot which has been rendered insoluble and neutral in the manner described above, the filtrate of silver nitrate solution is slightly acid, the maximum amount of acid which we have observed in the first 10 cc of filtrate was approximately 1 part in 10^5. This acidity decreases as successive portions of the silver nitrate solution are filtered through the pot. If the pots be entirely filled each time with the solution and the whole of the solution be allowed to filter through, the second filtrate shows less than one part in a million of acid. If now distilled water be filtered through the pores until the filtrate is again neutral and free from silver nitrate and the pot be allowed to dry, it again possesses the property of bringing about the formation of traces of acid in the first portions of silver nitrate solution filtered through it. This seems to indicate that the reaction (whatever its nature) whereby acid is produced is at most only very slight and very soon reaches a condition of equilibrium, but that when the products are completely removed this condition of equilibrium is disturbed and the reaction can repeat itself.

For the foregoing reasons the recommendation was made to filter at least three portions of electrolyte through the porous pots before using them in the voltameter for the first time, and for the same reasons it is not permissible to wash the pores free from silver nitrate after use; indeed, the pots are in their most resistant condition when the pores are kept saturated with the same electrolyte that is to be used in the voltameter. When a porous pot is prepared and kept in accordance with the foregoing specifications it is by far the most resistant porous septum which has yet been used in the voltameter.

With regard to the nature of the action whereby the very slight amount of acid is formed when pure neutral silver nitrate solution is filtered through a clean insoluble porous pot, we devoted considerable effort to the study of this question immediately after the effect was first observed and came to the conclusion (1) that the action was catalytic in nature and (2) that the final result was a very slight reduction of the $AgNO_3$ to metallic colloidal silver with the formation of an equivalent amount of nitric acid. The observations which led us to this conclusion may be summarized as follows:

1. The first portions of the filtrate show a very slight reduction of $\frac{N}{1000}$ $KMnO_4$ solution.[26] Since tests showed that nitrites were not present, and since we have shown that colloidal silver reduces $KMnO_4$ solution it seemed evident that this reduction was due to colloidal metallic silver. The second and third following filtrates show no such reduction (or acidity).

2. Clean insoluble porous pots exercise a reducing action upon at least one other substance besides $AgNO_3$, viz, chromic acid. This effect was first observed when cleaning porous pots with the chromic acid mixture. If chromic acid (of normal strength with respect to hydrogen) be allowed to remain in the pores for a day or so and then washed out the solution has a distinctly olive-green color indicating the presence of a chromic salt (i. e., Cr_2O_6 has been reduced to Cr_2O_3). The chromic salt may be precipitated as chromic hydroxide Cr $(OH)_3$ by ammonia. It was at first thought that this reduction must be due to dust or organic impurities in and on the pot but the effect could be repeated with the same pot after thoroughly washing out the acid until the conductivity of the purest water was unchanged by filtration through the pot and when the pot had been heated to bright redness in the electric furnace and the greatest care taken to subsequently exclude all dust and organic impurities. Furthermore, blank experiments with the same chromic acid in the same surroundings but not in contact with a porous pot gave negative results. Since these results were obtained we have learned that a somewhat similar phenomenon was observed by Tscheishvili[27] with solutions of potassium permanganate and asbestos filters. It is not shown, however, that this effect is due to a reducing action on the solution.

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[26] This effect of porous siliceous material upon silver nitrate solution is discussed by H. E. Patten (J. Phys. Chem., **14**, p. 612, 1910). This phenomenon and also the production of acid by the action of porous pots upon silver nitrate solution had been observed in this laboratory and the results had been discussed in a conversation between one of the present authors and Dr. Patten before the publication of the latter's article.

[27] J. Russ. Phys. Chem. Soc., **42**, p. 856, 1910.

3. Other explanations of the formation of acid by the filtration of silver nitrate solutions through the pores are not in agreement with the facts, as, for example, the possibility of a double decomposition of the silicates of the pot by interaction with $AgNO_3$ resulting in the formation of strongly hydrolysed (and therefore acid) salts of the bases of the silicates (e. g., MgO, Al_2O_3, etc.,) for such an action would not account for the presence of reducing substances in the filtrate. Likewise the possibility that colloidal AgOH is filtered out by the process, the hydroxide remaining behind on the inner wall of the pot is untenable, for this also would not account for the formation of reducing substances. Such an action as the above is known to take place with solutions of ferric salts.

The mechanism by which this catalytic reduction of $AgNO_3$ (and chromic acid) is brought about is a matter of conjecture, but this does not alter the facts in the least. Whether the reduction is brought about by the direct discharge of positive silver ions upon the negative walls of the pores or by the formation of some intermediate product (such as peroxides) which subsequently decompose, giving rise to the same end products can not be determined from the known facts.

3. ELECTROSTENOLYSIS

The foregoing phenomena offer a satisfactory explanation of possible electrostenolysis in the porous pot, i. e., deposition of metal by the current at points other than the primary electrode. The function of the porous septum seems merely to be that of any catalytic agent; that is the rate of the spontaneous decomposition of silver nitrate into metallic silver (which under normal conditions is inappreciable) is enormously increased by contact with a porous septum, resulting in the deposition of minute traces of metallic silver in the pores.

After some metallic silver (no matter how small an amount) has been formed in the pores, the stenolytic process proper, i. e., the increase in the amount of silver in the pores by the action of the electric current, is probably due to the silver being deposited on the cathode side of a particle (i. e., the side nearest the anode of the voltameter) at a greater rate than that at which it dissolves from its anode side. This difference in rate is probably due to the formation of silver peroxynitrate (Ag_7NO_{11}) or some other product which tends to render this side of the silver particle "passive."

This stenolytic action is, of course, dependent upon the current density through the pores, the potential gradient, and the percentage strength of the electrolyte. This action can at most be but very slight under working conditions; indeed, there is no experimental evidence that it occurs at all under the normal conditions in the voltameter, since the very slight amount of acid formed in the cathode chamber may be produced by the porous pot when no current is flowing. Moreover, the factors which cause electrostenolysis proper are identical with those which cause secondary reactions at the anode of the voltameter under normal conditions (i. e., high current density and dilute electrolyte). Therefore abnormal conditions of concentration and potential gradient which favor stenolysis would also affect the electrolyte around the anode in any nonseptum form and in exactly the same manner. It would seem, therefore, that any conclusions as to the possible evil influence of the porous pots under normal conditions deduced from the effects produced under the exaggerated conditions necessary for the production of stenolysis would apply as well to one case as to the other, so that in this respect no advantage can be argued for the use of a nonseptum form of voltameter. The disadvantages of nonseptum forms due to anode slime have been sufficiently explained.

Richards has shown that even in very exaggerated cases of electrostenolysis the weight of silver deposited is not appreciably affected. F. E. Smith has obtained lower values when the conditions were selected so as to produce pronounced stenolysis in the porous pots,[28] but entirely similar results would doubtless follow if the same conditions of dilution and fall of potential were purposely produced at the anode itself, so that this evidence does not condemn the porous pot. The only legitimate objection which can be urged against the porous pot is that it does produce a very slight catalytic action upon the electrolyte independently of the action of the current; but with porous pots prepared in accordance with the specifications given, this action is too slight to influence the weight of the deposit, as the results of the numerous experiments with the porous-pot voltameter show. On the other hand, if no septum whatever is used the difficulty of dealing with the anode slime and the possibility of the formation of base at the anode are quite as serious objections as those suggested above concerning the porous pots. Actual comparisons have shown that both of these possible sources of error are easily controlled in actual practice.

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[28] Private communication.

F. PURITY OF THE SILVER DEPOSIT

1. CONSTANCY OF ANY ERROR DUE TO INCLUSIONS

The possibility of the inclusion of foreign material in the silver deposits has been recognized since the time of Lord Rayleigh's work in 1884. Many attempts have been made to measure the quantity of such inclusions as well as to determine their nature. The results of different observers are contradictory. The work of the present authors has demonstrated that under proper conditions the average deviation of a single observation from the mean of a series can be made as small as a few parts in one hundred thousand.

TABLE 13

[Size of voltameter, large, medium, and small, are indicated by the letters lms]

Observations	No.	Voltameter	Mean value for cell	Average deviation of a single determination
First series	42	Porous pot (lms)	1.01828_7	6 in 100 000
Second series	44	Porous pot (s)	1.01827_6	3 in 100 000
Second series	18	Porous pot (lm)	1.01832	4 in 100 000
Third series	156	Porous pot (lms)	1.01826_7	3 in 100 000
Third series	55	Smith form (lms)	1.01827_4	4 in 100 000

The uniformity of the means as well as the smallness of the average deviations show that either there are no significant inclusions of liquid or other foreign matter in the crystals or else that such inclusions are very constant in amount. The deviations shown in the above table include many sources of error beside the inclusion in the crystals, such as errors in timing the deposit, the constancy of the current, washing and drying the deposit, besides the errors of weighing the bowls both with and without the silver deposit. It is not likely that in a silver crystal formed perfectly according to the cubic system or one of its modifications that any appreciable amount of inclusions would be possible. Colloidal particles, however, form nuclei for new crystals, and it seems plausible that the inclusions if present are caught between the crystals as they form. This would not happen often, however, in the case of pure electrolytes which contain very little colloidal matter. It is not necessary that we should know what the amount of the inclusions is so far as the measurement of the international ampere is concerned, since the defined electrochemical equivalent, 1.11800 mg per coulomb, is for the silver as we find it deposited in actual practice in the voltameter. But it is important, if possible, to eliminate any error due to the inclusions from an absolute determination of the electrochemical equivalent in order to compute the value of the faraday.

2. PREVIOUS DETERMINATIONS OF INCLUSIONS

Lord Rayleigh and Mrs. Sedgwick[29] made two attempts to measure the inclusions in their deposits. In the first place they dissolved deposits in HNO_3 and precipitated the silver with NaCl, comparing the results with pure silver obtained from Johnson and Matthy, but the results were inconclusive. They then tried heating the deposits to incipient redness, finding a loss of about 0.010 per cent in the deposits made from $AgNO_3$ and 0.1 per cent in the deposits made from $AgNO_3$ electrolytes to which acetate had been added. The results of our own work would lead us to expect in the former case an even greater loss than they found, since they were using the filter-paper voltameter. This is because the silver colloid formed by the action of the filter paper on the electrolyte tends to break up the crystalline structure of the silver as we have shown elsewhere[30], permitting greater amounts of the liquid to be included, besides organic matter from the paper itself. The smallness of their result may be readily explained by the assumption that they did not drive out all the foreign material. In case of the acetate the large loss is not surprising, since the presence of the acetate causes a very complete destruction of the ordinary silver crystals, and consequently much larger quantities of foreign material may be included.

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[29] Phil. Trans., 175, p. 411.

[30] This Bulletin, 9, p. 263.

Thomas Gray [31] on the other hand noted that deposits properly washed may be heated in a spirit flame without loss in weight.

Richards, Collins, and Heimrod [32] made an analysis of their deposits by dissolving the silver of a filter-paper voltameter in HNO_3 and precipitating with HBr. They found the mean deficit of silver to be 0.007 per cent, but by correcting apparent numerical errors in Nos. 35 and 36 of their table this is reduced to 0.002_6 per cent. Later Richards and Heimrod [33] redetermined the inclusions in the silver by heating the deposit to incipient redness. They give as the mean loss in weight 0.018 per cent, but note that it varies somewhat with the conditions of the experiment.

Van Dijk [34] heated the platinum crucibles with their deposits in an electric furnace. His conclusion was that the deposits, as ordinarily made, contain no appreciable inclusions, but if a deposit is made upon another deposit which has been heated to redness a considerable loss in weight is observed the first time the new deposit is heated. This he ascribed to fissures and cavities in the old deposit caused by the strains created when it was first heated to a high temperature. These cavities inclose liquid when the second deposit is made and they are sealed off by the new silver. Since 500° is sufficient to expel this liquid the first time the cup is heated, no further loss being detected on subsequent heatings, he concluded that none of the deposits can contain inclusions after being thus heated. In some cases he used a temperature as high as 600°. His experiments were chiefly on deposits made in the porous-cup voltameter.

Smith, Mather, and Lowry [35] tried heating a few deposits over a Bunsen flame and found no loss. They then accepted Van Dijk's results without question.

Jaeger and Von Steinwehr [36] heated a number of the deposits in the crucibles over a Bunsen flame; they found small losses which, however, were not as great as the crucibles suffered when empty. They therefore concluded that the inclusions are insignificant.

Duschak and Hulett [37] again took the matter up because of the contradictory results of Van Dijk and of Richards and Heimrod.

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[31] Phil. Mag., **22**, p. 399; 1886.

[32] Proc. Am. Acad., **35**, p. 138; 1899.

[33] Zs. f. Phys. Chem., **41**, p. 321.

[34] Arch. Neer. des Sci. II, **10**, p. 277; Ann. der Phys., **19**, p. 246.

[35] Phil. Trans., **207**, p. 570.

[36] Zs. f. Instr., **12**, p. 354.

[37] Trans. Am. Electro Chem. Soc., **12**, p. 257.

They placed a definite quantity of deposit in combustion tubing connected to a small manometer and sealed it off after drying the interior of the apparatus and evacuating it. When the heating of the deposit began an increase in the pressure was noted that progressed in stages as successively higher temperatures were reached until the maximum of about 600° was reached. In one experiment using a quartz bulb the temperature was carried up to the fusion point of silver, but the gas liberated after passing 600° was very small in amount. They condensed the water vapor in a capillary tube so that this could be distinguished from the other gases. They concluded that the total inclusions on the average were about 0.011 per cent, and that they were distributed throughout the crystals. In the case of deposits made in vacuo the inclusions seemed somewhat less.

The subject was again taken up in a paper by Laird and Hulett.[38] They made some modifications of the preceding method of which the most important was to alloy the silver with tin in order to reduce the temperature required for complete expulsion of the inclusions. They also endeavored to identify the substances given out, and from the amount of nitrogen found, to compute the amount of entrapped silver nitrate; but this method suffers from the disadvantage that errors necessarily present in so difficult a determination are multiplied by 12, since N:$AgNO_3$::1:12. Their main conclusion was that silver nitrate in appreciable quantities is present in the silver crystals, but probably does not exceed five parts in 100 000 for the best deposits.

3. EXPERIMENTS ON INCLUSIONS

At the Bureau of Standards

(a) *Detection of Silver Nitrate.*—For the estimation of the included silver nitrate the deposit after being carefully removed from the platinum cup was alloyed with fifty times its mass of pure redistilled mercury and the alloy then shaken up with double distilled water. Any silver nitrate present would be liberated by the alloying process and would dissolve in the water. We thought that even very small amounts could be detected by means of phenol sulphonic acid in the usual manner for estimating small amounts of nitrates. Some difficulty, however, was encountered in detecting in this way the small amounts of silver nitrate purposely added to silver amalgams to test the method. It was thought that the trouble was due to the presence either of silver or mercury salts or to both in the solution. Mercury displaces silver to a limited extent from aqueous solutions, a condition of equilibrium being reached in which both silver and mercury are present in the solution. Any mercury salts present in the solution must be in the mercurous condition because of the excess of metallic mercury present. Therefore to completely remove both silver and mercury from the solution it is only necessary to add a few drops of hydrochloric acid. This changes the nitrate present into nitric acid, in which form it can be readily estimated colorimetrically by the phenol sulphonic acid. Blank tests showed that quantities of silver nitrate corresponding to less than one part in one hundred thousand of the silver present in the amalgam could be easily detected and larger amounts could be estimated.

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[38] Trans. Am. Electrochem. Soc., 22, p. 345.

Several normal silver deposits were examined by this method for occluded silver nitrate, but only the faintest traces (less than 0.001 per cent) were found. It is therefore certain that any error due to included silver nitrate alone is entirely negligible in the case of our normal deposits from the purest electrolyte. It remained to be shown, however, whether this was also true for the abnormally heavy deposits from contaminated electrolyte, as, for example, the deposits from the filter-paper voltameter. Accordingly several of these were also examined in the same way, with the result that a very small but definitely larger amount of nitrates was found. In making the estimation, the color produced was matched with that formed by the addition of a known amount of standard silver nitrate solution to a thoroughly washed amalgam, all of the conditions as to dilution, temperature, etc., being exactly the same in the two cases. The amounts of nitrate found in the silver deposits obtained from the filter-paper voltameter varied from one to two parts in one hundred thousand. The error due to the inclusion of silver nitrate alone can not, therefore, be greater than one or two parts per hundred thousand even in deposits which are heavier than the normal deposit by as much as ten to forty times this amount.

(b) *Estimation of Included Water and Volatile Material.*—It appeared from the foregoing results, therefore, that if the excess (Δ) in mass of the deposits from the filter-paper voltameter over those from the Richards type is due to inclusions (of some kind), they must consist of some impurity other than silver nitrate itself. Water seemed the most probable single inclusion other than colloidal silver which could be present in amounts sufficient to account for the greater portion of this excess; for the electrolyte immediately next the cathode where the silver is being deposited must necessarily be much more dilute than the average concentration of the whole electrolyte. It seems highly probable that the inclusions (if present at all) must have practically the same concentration as this depleted electrolyte. This would mean that the deposit from an electrolyte of an average concentration of 8 per cent (such as may be present in the cathode chamber of the small size Richards voltameters) would consist of not less than 92 per cent water, the more probable value being something like 95 to 98 per cent or even greater.

Accordingly experiments were planned to determine with the greatest possible accuracy the total amount of water included. The indirect method of noting the loss in weight of the silver crystals when they are alloyed with some nonvolatile metal was finally decided upon as the most practical way of accomplishing this result.

A careful consideration of all the nonvolatile metals which might be used for this purpose led to the selection of platinum as the most suitable. Accordingly, arrangements were made to alloy the silver deposit with the platinum crucible in which it was originally deposited, making very careful weighings to determine any loss in weight.

The heating was done by means of a good alcohol flame, and the change in weight of the crucible alone (heated in the same manner as when alloying the silver) was carefully determined before the silver was deposited in it. Likewise after alloying the silver, the crucible was again heated to determine whether the weight had become constant. The question of the volatility of the silver under the conditions could thus be accurately checked.

To facilitate turning the crucible while in the flame in order to completely alloy every portion of the silver, a handle of stiff platinum wire was fused to the crucible so that it could be readily handled with platinum-tipped tongs. A tightly fitting platinum cover for the crucible was kept in place during the heating and only one part of the crucible was heated at a time, so that there was always a large cool surface to condense any silver vapors which might volatilize.

The time available for this part of the work permitted the carrying out of only a single determination, the results of which are given below. The deposit alloyed was from electrolyte strongly contaminated with filter paper. This was purposely chosen for this first experiment because it was thought the loss in weight would probably be larger than from a normal deposit. Also it should throw some light on the question as to whether the excess mass is due mostly to occlusions or to colloidal silver itself. In the event that the former case proved true, our first conclusion that the principal rôle of the colloid is in breaking up the crystalline structure of the silver deposit, so that more electrolyte is included, would be confirmed.

Platinum cup empty:	mg
Loss of weight after first heating (10 min.)	0.075
Loss of weight after second heating (10 min.)	.001
Loss of weight after third heating (10 min.)	.009

Loss after first heating was probably due to some volatile material on the surface of cup before being used.

Platinum cup with silver:	mg
Weight of silver deposit	1093.920
Excess weight over pure deposit	0.560
Loss after alloying with platinum	0.536
Change (gain) after second heating	0.030

The process of amalgamation consumed more time than we had anticipated, hence we again heated the cup as before for about the same time (one hour), but found only a very small change.

The almost exact equality between the loss in weight upon alloying and the excess weight (Δ) of the deposit over the normal deposit would seem to indicate that the inclusions in the normal deposit are negligible.

(c) *Estimation of Organic Material.*—We have already discussed this in Part II of this series of papers. (See Vol. 9, p. 241.) Any of this material would of course be consumed in the alloying process given above for determining the presence of water.

(d) *Titration of the Silver Deposits.*—The ease with which we succeeded in making the silver estimations of small deposits when studying the acid effect led us to try to extend the method to titrate larger deposits. We hoped that by standardizing our ammonium sulphocyanate solution against some of our best electrolytic silver we might sucessfully measure the difference in silver content of a pure and an impure deposit. The indicator was prepared according to the method of Hoitsema.[39] We did not succeed as well as we had hoped, however, since the end point was transient when the samples of silver were more than one or two-tenths of a gram. We therefore were obliged to abandon the effort.

(e) *Conclusion.*—We do not regard the matter of inclusions in the silver deposits as satisfactorily settled. We believe that in the best deposits they are very small, probably less than 5 parts in 100 000, as estimated by Hulett. Our determinations of the silver nitrate present in the crystals are unfortunately directly opposed to his, so that for lack of further evidence we can not decide this point. The work of one of the present authors (Vinal) jointly with Dr. Bates, of the University of Illinois, on a comparison of the silver and iodine voltameters for the measurement of the faraday emphasizes the desirability of investigating the inclusions further. The value for the faraday is computed and discussed in their paper.[40]

G. REVERSIBILITY OF THE SILVER VOLTAMETER

In some of the earliest researches on the silver voltameter the current was measured by the loss in weight of the anode as well as the gain in weight of the cathode. This was true of Mascart's and Gray's work, but the differences tolerated in those days were greater than is considered permissible to-day. If Faraday's laws of electrolysis hold strictly for the silver voltameter there should be an equivalence between the loss of silver at the anode and the gain at the cathode, but with the advent of the complex ion theory no further efforts were made to measure quantitatively the changes taking place at the anode. Washburn and Bates[41] reflect the current opinion when they say "The reaction in the silver coulometer is not reversible."

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[39] Zs. f. Anorg. Chem., **17**, p. 647; 1904.

[40] This Bulletin, **10**, p. 425; 1914 (Reprint No. 218).

Since our work has shown that the complex ion heretofore ascribed to secondary reactions at the anode is probably nonexistent and that the effects supposedly produced by it are due to colloidal particles either present in the electrolyte or produced by substances (such as filter paper) introduced into the electrolyte, it seemed worth while to investigate further the question of reversibility.

Before making any quantitative experiments we began by considering the acid and potential changes taking place in the voltameter during the progress of an experiment. For this purpose it was most convenient to use as an anode the silver coating on the inside of a platinum bowl the electrolyte in which was connected through a siphon with that in a second bowl serving as cathode. This facilitated taking samples of the anode and cathode liquids for acidity tests and also measuring the potential changes between the bowls and some reference points which were fixed at the end of the siphon. With such an anode the liquid was in contact with both silver and platinum as in the case of the cathode. In the latter we know that after the deposit begins the current flows solely to the silver crystals, so that the question at once arose whether the current passing from the anode solution would do so from the silver crystals alone. This was found to be true provided that the amount of silver was not too small. It was easily proved by the absence of silver peroxynitrate crystals and by the absence of an increase in acidity of the anode liquid almost to the end.

Samples of the electrolyte for acidity tests were taken at stated intervals and the potential differences were measured on a high resistance potentiometer between the platinum cups and the ends of the siphons where fine silver wires dipping into the electrolyte were fastened. The results of these experiments are best shown graphically, and in the accompanying curves (Figs. 6 and 7) we give the acidities and potentials plotted as ordinates against the amount of silver remaining on the anode bowl as

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[41] J. Am. Chem. Soc., 34, p. 64; 1912.

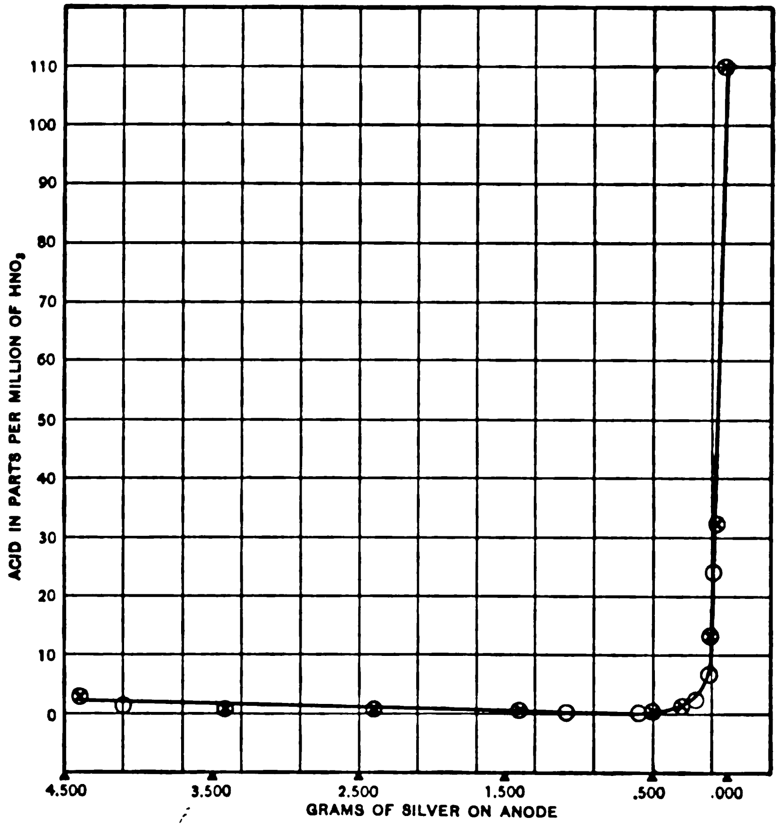

Fig. 6.—*Changes in acidity of anode liquid*

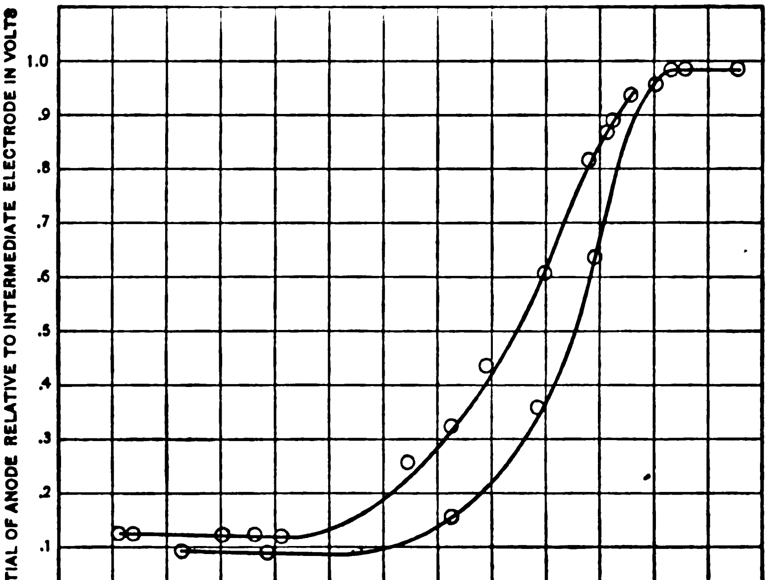

Fig. 7.—*Changes in potential of anode*

abscissa. This is of course a function of time and current. In the experiments we have kept the current as constant as possible under the circumstances so that we might compute the silver remaining on the anode from the time of taking the observations. The abscissa marked "0.00" represents the theoretical exhaustion of silver according to the equation $M = 1.11800it$, M being the mass of silver taken off the anode in milligrams and i the current in amperes and t the time in seconds. This is not, however, strictly true, since the secondary reactions begin when the break in the curve comes. This means that current is passing into the solution from the platinum surface with the formation of Ag_7NO_{11} crystals which speedily become visible. Consequently at the abscissa "0.00" some silver is still to be seen on the anode bowl.

Fig. 6 shows the results of two experiments (indicated by the crosses and circles, respectively), made to determine the relation of the acidity of the anode electrolyte to the amount of silver remaining on the anode. The crosses represent observations when the current was one-fourth ampere and the circles when the current was one-third ampere, but there is no difference between them. Fig. 7 gives the curves for the potential of the anode relative to an intermediate electrode. For the left-hand curve the current was one-half ampere and for the other one-third ampere. The anode was always positive with respect to the intermediate electrode. The slight initial decrease in potential was due to the small increase in temperature of the electrolyte before a steady state was reached. The maximum potential difference occurs at about the time of theoretical exhaustion of the silver on the anode.

Fig. 8 gives the complete data regarding both anode and cathode changes of one experiment using a current of one-half ampere. One doubtful observation on the anode acidity has been omitted as there is some reason to believe that it was confused with a sample taken from the cathode. The characteristics of the acidity and potential curves for the anode are about the same as in the preceding curves. The cathode curves II and IV show relatively uniform conditions to hold throughout the experiment.

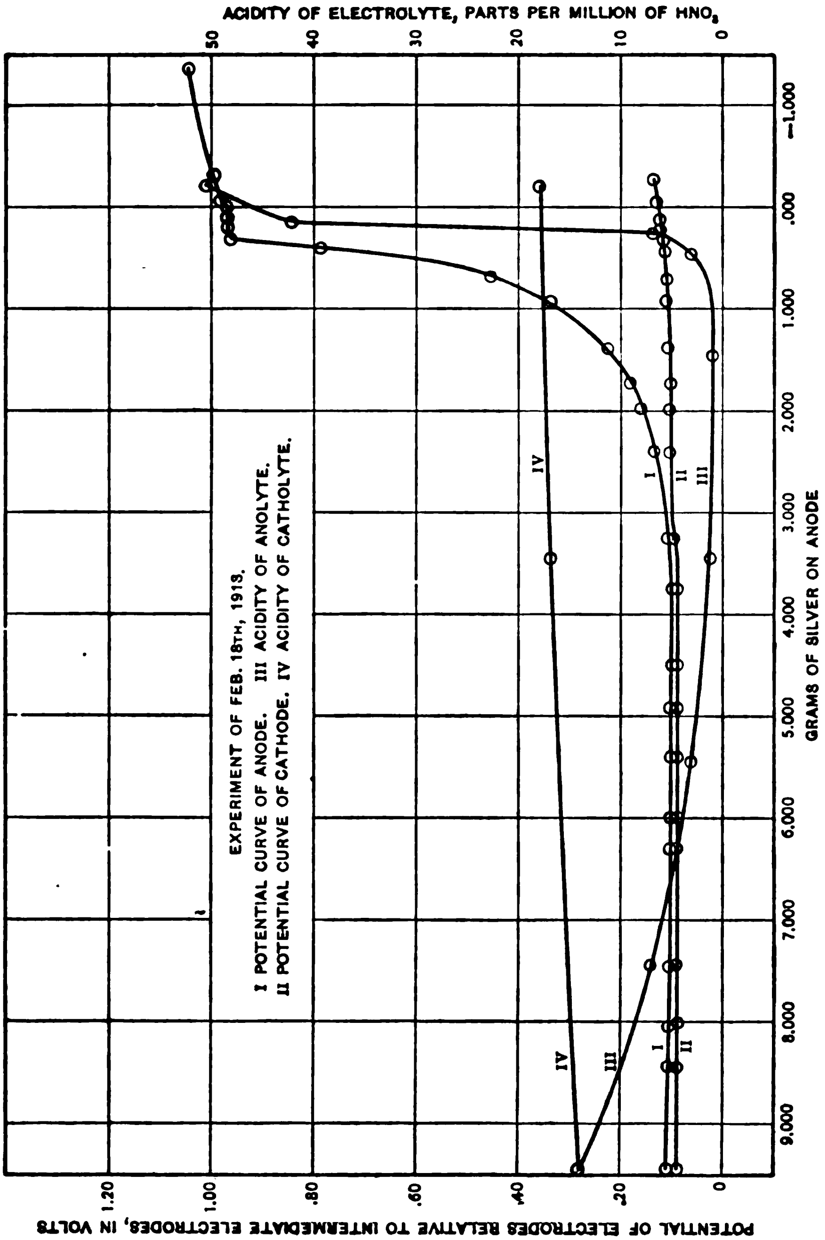

Fig. 8.—*Acidity and potential curves for both anode and cathode*

Having completed these experiments we were in a position to know under what conditions we might expect the voltameter to be reversible. In the first place a large anode surface was desirable to reduce the slime, and in the second place we saw that the amount of the silver on the anode bowl should not fall below 2.5 or 3 g. We accordingly prepared deposits from the best electrolyte in two of the large bowls to serve as anodes and carefully weighed them. Other bowls (empty) were prepared and weighed to serve as cathodes. Siphons connected the anodes and cathodes.

The results of two experiments were as follows:

TABLE 14

Date	Weight of silver on anode bowl	Current	Loss at anode	Gain at cathode	Deposit in standard Smith form
	g	amp	mg	mg	mg
Feb. 27, 1913	8	0.500	2164.81	2164.78	2164.81
Mar. 11, 1913	9	.500	2092.12	2091.92	2091.83

It will thus be seen that the agreement of the loss at the anode with the gain at the cathode is about the same order as for standard voltameters, so that we may say that under these conditions the silver voltameter is reversible. This indicates a nearer approach to a simple reaction according to Faraday's laws than has been before thought likely. It also argues that for pure electrolytes the inclusions are negligible.

One further question arose in connection with this work and that was the effect of using an impure anode. It was hoped that by reversing the voltameter as above, using an anode that was strongly striated that the difference between the loss at the anode and the gain at the cathode might give some data on the inclusions. Accordingly, in the experiment of March 11 we used a large cup containing a striated deposit of about 9 g, which was more than 8 mg excess over its mate made from a pure electrolyte. It was connected by a siphon to a second cup serving as cathode and the whole filled with pure electrolyte. The experiment had not proceeded far before there was a marked difference in the appearance of the anode bowls. That containing the pure deposit remained white and at the end contained little anode slime while the other turned dark and at the end contained an abundance of fine brownish slime that made great trouble in washing the bowl, as we have already described on page 500. All this slime which could possibly be recovered was put back in the bowl. After washing it was dried and weighed. The results were as follows:

	mg
Anode lost	2095.43
Cathode gained	2092.21
Standard Smith form	2091.83

The conclusion leaves no room for doubt that the purity of the anode is essential in such an experiment. The excess of its cathode over the standard form, which from the other cathode appears a little low (Table 14), suggests that such impurities as were contained in this anode may influence the deposit on the cathode, as we have already suggested more at length on page 500.

H. A SIMPLE VOLTAMETER OF SMALL COST

It seemed worth while to design if possible a form of voltameter which would give a fair degree of accuracy, but at the same time be an inexpensive instrument for general use. The anode was made in the form of a large ring set in a glass dish containing the electrolyte. This silver ring was made large to minimize the difficulties with the anode slime. The cathode was a small platinum ring resting in a shallow glass dish submerged in the electrolyte and so arranged that the whole might be lifted out together. As this platinum ring weighed only 10.5 g, the largest item of expense was reduced to about one-tenth that of the large size standards. It is not intended that this form should be used in any work requiring the highest precision, but the following comparisons show that it may be relied on to a few hundredths of 1 per cent. The arrangement of the parts is shown in the accompanying drawing (Fig. 9):

Date	Approximate time	Approximate current	Deposit in standard	Deposit on the ring	Difference
	sec	amp	g	g	
July 29, 1912	3615	0.510	2.04734	2.04748	$\frac{-7}{100\,000}$
Aug. 1, 1912	3615	.510	2.04879	2.04860	$\frac{+9}{100\,000}$

IV. VOLUME EFFECT

In our third paper[43] we have described a phenomenon which we have designated as the "volume effect." This is manifested in the case of impure electrolytes by an increased weight of deposit in the large bowls over that in the small bowls, used simultaneously, the excess of the former being roughly proportional to the difference in volume of the cathode liquids in the two sizes. By learning how to purify the electrolyte we overcame the difficulty. As the results given in this paper show, the large and small sizes agree when the electrolyte is pure. We regard this volume effect as a valuable test of the purity of the electrolyte. We had not intended

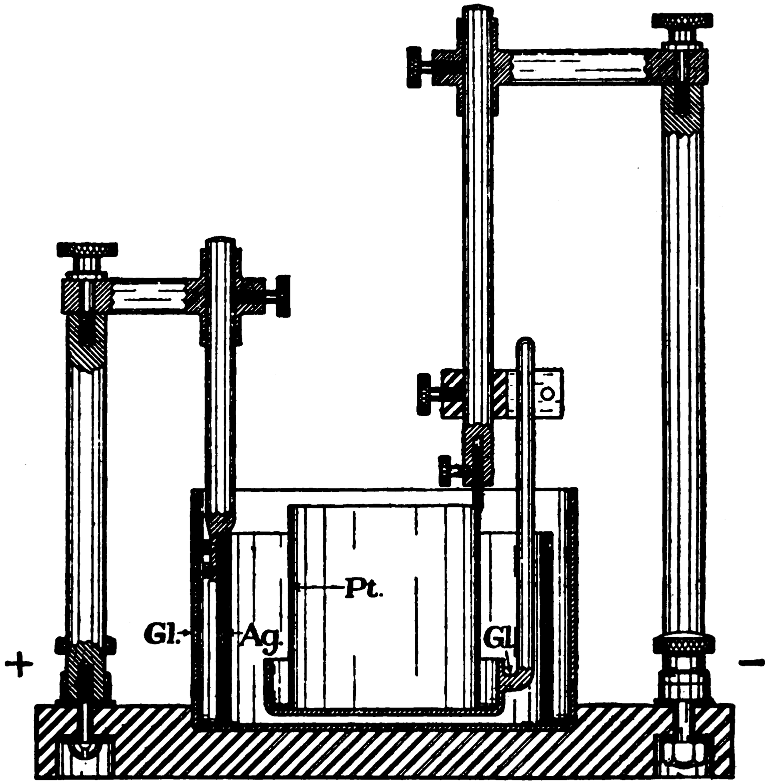

Fig. 9.—*A voltameter of small cost*

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[43] This Bulletin, 9, p. 514 (Reprint No. 201).

to discuss this matter further until specifications are adopted, but a recent paper by von Steinwehr [43] seems to call for some further discussion. He says: "We are drawn to the opinion that if the reality of the volume effect may have been established it is, after all, very extraordinary that it has been only observed with the porous-pot type and not to appear in the other types also. It naturally follows from this that this effect is not to be sought in the originally present impurities in the solution, but in the porous pot itself." We have previously discussed this question at some length [44] and have shown that the volume effect has been observed in other forms of voltameter. We have also given [45] good experimental evidence that a suitable purification of the electrolyte will eliminate the volume effect.

Going back 30 years, we find evidence of the volume effect in the work of Lord Rayleigh and Mrs. Sedgwick,[46] who used the filter-paper voltameter. Examining their Table II we find that, averaging all their differences between large and small voltameters for all the observations used for computing the final value, that the deposit in the large cups exceeds that in the small cups by 14.5 in 100 000, and only in one case out of 10 does the deposit in the small cups exceed that in the large cups. We were not the first to recognize this difference since Schuster and Crossley [47] called attention to it in 1892 and tried to explain it. They say: "A second anomaly lies in a small but regular discrepancy in the deposits when they are taken simultaneously in platinum bowls of different sizes." Their results are given in their Table I (p. 347). In only one observation, which is very discordant with the others, does the deposit in a small bowl exceed that in the large bowl. The mean excess of the large bowls over the small bowls for the other seven observations is 17 parts in 100 000. They say: "* * * the results give a consistent difference of about 2 parts in 10 000 in favor of the large bowl."

The volume effect is also to be observed with the siphon voltameter as pointed out in our third paper.[48] Indeed, von Steinwehr calls attention to the large values obtained using siphons by Kohlrausch and Laporte, but in each case he adds that it is due to some hitherto unexplained error! In conformity with these observations our own show the mean value of 10 siphon observations to be 1.01858 volts for the Weston cell at 20°, which is 30 parts in 100 000 over the value as determined by the porous-cup voltameter in the same series of measurements. This difference can not be attributed to experimental error. Moreover we have shown in this paper [49] that we have brought the siphon voltameter nearly into agreement with the porous pot and Smith forms by purifying the electrolyte to the highest degree, as we know how to do now. The mean value of five siphon voltameter determinations of the cell given in this last paper is now 1.01832, or 26 parts in 100 000 lower than before obtained, using unpurified electrolyte in the same cups and with the same siphons. Such differences can not be accidental. Further evidence on the volume effect in the siphon form is found on pages 156 and 165 of the Report of the International Technical Committee. The experiment of May 10 included six voltameters of the siphon form, as well as several other standard forms. The electrolytes used were from three sources. That designated as A was prepared by Mr. F. E. Smith of the N P L and was believed to be the purest; that designated as B was as purchased from Poulenc and our tests showed it somewhat impure; that designated as "Old Baker" was found by tests to be the most impure of all. Expressing the results in terms of the mean of all the voltameters taken as unity we find the relative weights, as given in the first part of the table, page 156, as follows:

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[43] Zs. f Instrk, **33**, p. 321; 1913.

[44] This Bulletin, **9**, p. 514 (Reprint No. 201).

[45] This Bulletin, **9**, pp. 514–517 (Reprint No. 201).

[46] Phil. Trans., **175**, p. 438; 1884.

[47] Proc. Royal Soc., **50**, p. 344; 1892.

[48] This Bulletin, **9**, p. 516 (Reprint 201).

Electrolyte	Relative weight	Mean
A	1.00000 1.00000	1.00000
B	1.00028 1.00014	1.00021
Old Baker	1.00023 1.00037	1.00030

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[49] This paper, p. 492.

Or compared with the Smith form taken as standard, as on page 157, we find these results as follows:

Electrolyte	Relative weight	Mean
A	1.00012 1.00012	1.00012
B	1.00026 1.00040	1.00033
Old Baker	1.00049 1.00035	1.00042

The obvious conclusion in any case is that the electrolytes gave volume effects in the order of their estimated impurity.

As to the volume effect in the new form no conclusions can be drawn from Table XLVIII, as given by the International Committee, since Mr. Smith did not use an impure electrolyte in a small size of his voltameter, but data is available in Table No. 7 of miscellaneous results given in the present paper. On July 17, 1911, we used an electrolyte as purchased from Baird and Tatlock. This showed a volume effect in both the porous-cup form and the new form, and again on December 14 an electrolyte yielding an abnormal result in the porous-cup form showed a volume effect in the Smith form also. We believe that enough work has been done to show that the volume effect is not confined to the porous-cup form.

Dr. von Steinwehr lays particular stress on three "objection-free" observations contained in Table XLVIII of the report of the International Committee which show small values in large voltameters for electrolyte believed to be impure. But it is impossible to prove that the volume effect is a porous-pot phenomenon from these three "objection-free" observations since two of them were made by Prof. Laporte using Smith's new form of voltameter, as can be seen by reference to the original tables, while the third was made in a porous-cup voltameter by Prof. Laporte using a very small anode, as may be seen by referring to page 148.

We now come to the question of whether the reproducibility of the porous-pot voltameters is sufficient to prove the reality of the difference between the large and small sizes. Dr. von Steinwehr denies that it is. He points out that the average difference between large and small voltameters in our first series is only 2.5 in 100 000. He would be quite right in saying that we had not proved our point if our evidence rested on this alone. At this time we were using the largest size of porous cup shown in Fig. 2 of our first paper, in the large-size bowls. The bulk of these porous cups so diminished the volume of cathode liquid that its excess over that in the small bowls was not great and hence only a small volume effect would be expected. The volume effect depends of course on the difference in the volumes of the electrolyte in the cathode space, and not on the difference in the sizes of the bowls. We did not discover the volume effect until we began using the smaller porous cups in the large voltameters (second series).

Then we carried the computations back for the first series and found the difference 2.5 in 100 000 recorded above, which, while small, is in the direction to be anticipated. The second series of measurements mentioned by von Steinwehr are of little interest, since all the experiments in which large and small voltameters are compared have been separately tabulated in Table 9 (supplement to report of International Technical Committee), which he calls the third set of observations. In this it is shown that the mean of the large cups exceeds the mean of the small cups by 7 parts in 100 000. However, von Steinwehr does not consider the reproducibility of the voltameter good enough to prove this. If there were no volume effect it would be reasonable to suppose that in half the experiments the deposits in the small voltameters would exceed those in the large sizes, but this is not the case. The deposits in the large voltameters exceed those in the small sizes in every case.

Accidental errors are bound to enter into the observations and hence we must compute a mean result, which is mathematically better than the result of a single observation by the square root of the number of observations. When a difference is observed always in the same direction it can not be called an accidental error. We have shown in Table 7 of the supplement to the international technical committee report that the average reproducibility of the small porous-cup voltameter is $\frac{1}{100\ 000}$, or the average deviations in various runs is 3 in 100 000, yet von Steinwehr comments on the "not very great consistency" of our results when his own results given in Table 5 of his 1908 paper shows his average variation using the Kohlrausch voltameter to be about 9 parts in 100 000 and with the porous-pot form about 8 parts in 100 000. These average deviations, as will be seen, are between two and three times as large as have entered in our work.

Referring to page 338 of von Steinwehr's 1908 article we find that the maximum amount of electrolyte used was 95 cc, which corresponds almost exactly to our smallest size of voltameter. We think if he had used larger sizes of voltameter (about 350 cc), such as have been used by the N P L, L C E, and B S, that he would have found the volume effect himself. Satisfactory tests for the volume effect can not be made without using bowls differing considerably in volume. Such small bowls as used at the Reichsanstalt would not be expected to show it.

V. CONCLUSIONS AND SUMMARY

This paper concludes the experimental work which has been done at the Bureau of Standards on the silver voltameter as an international standard. Some further work on a few remaining problems including the determination of the purity of the deposited silver has been planned, but will be done elsewhere. In this, the Bureau will cooperate. The measurement of the Faraday has been carried out jointly with Dr. S. J. Bates, of the University of Illinois, who used the iodine voltameter simultaneously with the silver voltameter at this Bureau. The results of this work are to be published shortly.

Following this paper we shall publish a general summary of the work done here with the object of presenting the recent developments as concisely and completely as possible. We shall also include our draft of proposed specifications which are the natural outcome of our work, trusting that they may be of value when the international specifications are formulated for general adoption.

The principal points considered in the present paper are:

1. A determination of the voltage of the Weston normal cell using the porous cup and the Smith form voltameters. These are

found to be in substantial agreement and give the value 1.01827 volts at 20°.

2. A study of the effect of acid in the voltameter has shown a quantitative relation expressed by the equation $y = -4.5x + 0.02x^2$ to hold between the acidity of the electrolyte (x) and the resulting decrease in deposit (y) both expressed in parts per million, provided the electrolyte is pure. If the electrolyte be impure, the results can not be predicted.

3. We have studied the influence of septa other than filter paper and have found the porous pots made by the Königlich Porzellan Manufaktur when properly prepared and used to be a safe and efficient separator of anode and cathode.

4. We have made some experiments on the inclusions of the deposited silver and conclude that when pure electrolyte is employed no appreciable inclusions exist.

5. We have found the conditions under which the silver voltameter may be said to be reversible so that the current may be measured by the loss of the anode as well as the gain of the cathode. This is scientifically interesting since it adds to the evidence already obtained to disprove the heavy anode ion theory, but is of little practical importance.

Finally, we believe that the silver voltameter has shown itself to be an instrument of precision and capable of checking the constancy of the Weston normal cell according to the decision of the London conference.

WASHINGTON, December 1, 1913.

INFLUENCE OF ATMOSPHERIC CONDITIONS IN THE TESTING OF SUGARS

By Frederick Bates and Francis P. Phelps

That atmospheric conditions may exert an appreciable effect in the testing of sugar has been vaguely recognized for some years. The magnitude of this influence has, however, never been determined, and it is difficult to understand how this possible source of error has so long been practically ignored when we consider the large amount of research that has been carried on in an effort to reduce the process of testing to an exact science. Fortunately in the standardization of the saccharimeter, by means of the normal solution of sucrose, all chance of error from atmospheric conditions is eliminated. The normal weight of sucrose is made up to volume, and the polariscope tube is filled, under conditions that eliminate an appreciable change in the concentration of the unfiltered solution. In the process of testing, these conditions are unavoidably altered. The necessity for clarification requires that the liquid be passed once, and frequently twice, through ordinary filter paper to remove the precipitated impurities. While this is being done, there is more or less exposure to the atmosphere of the laboratory, with a consequent increase in the concentration. Since the rotation observed is directly proportional to the concentration, any change, if appreciable, must either be prevented or a correction applied to the polarization. Browne[1] and other investigators have recommended the use of cover glasses on the funnels to guard against possible evaporation.

The process of testing should obviously be such that when applied to the normal sucrose solution the polarization will be 100 on the saccharimeter scale within the limits of accuracy prescribed by other sources of error. With the object of accomplishing this, the suggestion has recently been made that the normal solution should be filtered in the determination of the 100° S point. Since atmospheric conditions vary greatly from day to day, such a procedure would be futile. On the other hand, the suggestion has been made that the 100° S point be set high. It has been shown by Bates and Jackson,[2] who have made an extended investigation of the 100° S point, the final results of which are now ready for publication, that the present basis of standardization of the saccharimeter is such that all near normal sugar solutions polarize approximately 0°.1 S too low; that is to say, the present 100° S point is approximately 0°.1 too high. In view of this fact, the suggestion has been made that the present value of the 100° point be left where it is, in order to allow for an increase of that magnitude in the polarization in ordinary testing, due to an increase in the concentration. This proposition, in our opinion, is untenable from a scientific standpoint, because it presupposes a constant effect of 0°.1 sugar, which is obviously not to be expected. The results of our investigation show that atmospheric conditions frequently introduce a relatively large error and that this error can always be eliminated.

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[1] Browne: Handbook of Sugar Analysis, p. 205.

The factors which influence the rate of evaporation from the surface of a liquid are numerous and the range of conditions under which this phenomenon occurs is so extensive that these factors may have a relatively wide variation in their magnitudes. In the greater part this accounts for the difficulty experienced by investigators, from the time of Dalton, in deriving a formula which adequately gives the rate of evaporation under all conditions in nature. Perhaps the most consistent formula is that of Marvin,[3] which takes the following form:

$$\frac{dQ}{dt} = \frac{C}{B}(P_{as} + P_s - 2P_a)f(P)\varphi(V). \tag{1}$$

in which

dQ = quantity of water evaporated in time dt.

P = general symbol for vapor pressure.

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[2] Orig. Com., 8th Int. Cong. of Applied Chemistry, 25, and Bureau of Standards Bulletin, 10.

[3] Marvin: Monthly Weather Rev., February, 1909, 37:58, eq. 6.

P_s = saturation vapor pressure at temperature of water surface.

P_{as} = saturation vapor pressure at temperature of air near the water.

P_a = saturation vapor pressure at the temperature of the dew point in the air near the water.

B = barometric pressure.

V = velocity of wind.

C = constant.

Marvin states that the data available are as yet insufficient to evaluate the constant factors or to give the exact form of the terms depending on wind and atmospheric moisture. However, it is possible under certain conditions to solve (1) obtaining $\frac{dQ}{dt}$ with ample accuracy for special cases. In general the predominating variable factor in determining $\frac{dQ}{dt}$ is $(P_s - P_a)$, commonly designated the potential head. If we consider the special case of evaporation of water from a small vessel in the laboratory, a considerable simplification results. The influence of barometric pressure, as well as that of $f(P)$ and $\varphi(V)$ becomes negligible; and $(P_{as} + P_s - 2P_a)$ reduces to $(P_s - P_a)$ under the permissible assumption that $P_{as} = P_a$; that is, that the air near the water surface is practically saturated at a temperature near the dew point, a condition roughly realized in the absence of ventilation.

The term $f(P)$ in (1) is somewhat indefinite. It was inserted by Marvin to provide for the contingency that under certain conditions the evaporation would not be strictly linear with the potential head. Just what form it might take is problematical. Fortunately, in our experiments, the conditions were such that it seemed probable that a straight-line relation would hold within the experimental errors of the observations. The experimental data given below fully sustain this conclusion.

We may then write

$$\frac{dQ}{dt} = CA(P_s - P_a) \qquad (2)$$

or

$$Q = CA(P_s - P_a)T \qquad (3)$$

where A is the area of the exposed surface. It will be observed that (2) and (3) cover the cases of zero and negative evaporation, the latter occurring when the temperature of the water is less than the temperature of the air at the dew point. We will show in what follows that (2) and (3) are directly applicable to the change in the concentration of the sugar solution, which ordinarily takes place in the testing of sugars.

METHODS USED

The area of the liquid from which evaporation can occur is constantly changing during the filtration. The total exposure is, however, the same for similar filtrations and the area, A, in equations (2) and (3) may consequently be taken as unity. If, then, we determine the constant C experimentally, we can calculate the evaporation for any potential head. Obviously, C may vary with the time of filtration, the rate of diffusion, the nature of the exposed surface, etc. It is nevertheless a constant for any particular set of similar filtrations.

We have utilized two methods for determining the change in concentration. The first tried was that of weighing the solution during filtration. The second, that of noting the change in the polarization. Since the polarization is directly proportional to the concentration, the change in polarization is proportional to the amount evaporated. $\frac{dQ}{dt}$ or more strictly, in the experiments, $\frac{Q}{T}$ thus has proportionate numerical values in both methods, provided the loss by evaporation is small as compared with the total quantity of solution. The loss in grams by weighing is equal to the increase in degrees sugar in the polarization. For convenience we have adopted the minute as the unit of time throughout our experiments.

In determining the potential head, P_a was calculated from the vapor-pressure tables for water, the necessary data being secured by means of the psychrometer referred to below. P_s is taken as the vapor pressure of water at the observed temperature of the solution. The lowering of the vapor pressure of the solution due to the presence of the sugar is negligible. At 30° C it amounts to 0.6 mm, which is equivalent to a change in the polarization of

0°.0006 sugar per minute. In all the experiments the normal solution—26 grams in 100 cc—was used.

APPARATUS

In order to carry out the experimental work it was found desirable to have control, during the filtration, of the atmospheric conditions over a wider range than would ordinarily occur in the average laboratory during a cycle of 12 consecutive months. This was made possible by the use of a constant temperature room with a content of about 15 cubic meters. The room was, in reality, a large thermostat, having a considerable range of accurate temperature adjustment. The air was kept thoroughly mixed by an electric fan which discharged over a false ceiling perforated with a large number of openings. Since equations (2) and (3) are based upon the elimination of the wind factor, (V), of equation (1), care was exercised to eliminate appreciable air currents. Tests with a sensitive anemometer showed this condition to be satisfactorily attained.

The moisture content of the air was regulated by freezing out some of the vapor by means of a brine coil or by admitting steam into the room, according as the amount of moisture present was greater or less than that desired.

The required temperature was maintained by an electric heater controlled by a mercury interrupter with a toluene coil, the maximum variations being about 0.3° C for any point between 15° C and 40° C. When once a given air condition had been secured it could be maintained indefinitely within satisfactory limits.

Any relative humidity between 17 per cent and 92 per cent could be attained at any temperature between 18° C and 39° C. Any desired potential head (P_s-P_a) could thus be obtained between 4 mm and 41 mm of mercury. An Assmann psychrometer was used for making all measurements of the amount of moisture.

The weighing experiments were made upon a large balance open to the atmosphere except while a weighing was being made, and sensitive to $\frac{1}{5}$ mg with a load of 200 g. The funnel and cylinder were placed directly upon the scale pan.

For making the polarization measurements, the Bates type of saccharimeter with adjustable sensibility was available. It was inclosed in a small thermostat, thus insuring a constant temperature during measurements. In order to secure a high degree of accuracy in the polarizations, the half-shadow angle was set at 3°. The light source was a Nernst lamp of 500 cp. The Bates type, 200 mm, metal polariscope tubes were used. The corrections for length were determined by the division of weights and measures of the Bureau of Standards. The glass funnels were stemless and had a diameter of 90 mm. The cylinders had a diameter of 40 mm and a height of 125 mm. The plaited type of filter with a diameter of 18.5 cm was used. Tests made on raw sugars when the smooth filters were employed gave results identical with those on the plaited type.

EXPERIMENTS WITH REFINED SUGAR

In the beginning of the work it was believed that the research could be satisfactorily consummated by the use of the best refined commercial sugar and that the results would be equally applicable to all sugars. This was desired because of the relative ease of manipulation and the avoidance of clarification.

The first experiments were made by the method of weighing. The solutions were made up at the temperature at which the tests were to be made. A clarifying reagent was not added. No cover was placed over the funnel. In order to retard the filtration so as to make the conditions comparable to those existing when raw sugars are tested, the bottom of the funnel was plugged with absorbent cotton. This effectually increased the time required for the solution to filter. In order to measure the total evaporation a solution was placed upon the pan of the balance and weighed at intervals of a few minutes until all had filtered through. The average amount lost per minute, $\left(\frac{Q}{T}\right)$, by evaporation was then calculated. This was repeated for different conditions of temperature and humidity in order to secure data over a wide range of potential heads. Sufficient data was thus secured to solve equation (2) for the constant C. The results are given in Table 1. Taking the average of the values of C we have

$$\frac{Q}{T} = 0.0013\ (P_s - P_a) \qquad (4)$$

which gives the evaporation per minute under these conditions for any potential head. Column 6 gives the total loss in weight during the entire filtration. Columns 7 and 8 show the agreement between the observed evaporation and that calculated from equation (4). The results are shown graphically in Fig. 1.

TABLE 1

Refined Sugar; Funnel not Covered; Determinations by Weighing

$$\left[\frac{Q}{T} = 0.0013\ (P_s - P_a)\right]$$

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 $P_s - P_a$ mm of Hg	6 Total change	7 Observed $\frac{Q}{T}$, grams per minute	8 Calculated $\frac{Q}{T}$, grams per minute
°C	°C	°C	Per cent		g		
21.1	20.8	17.4	71.8	5.50	0.407	0.010	0.007
20.5	20.2	16.6	69.8	5.66	0.182	0.009	0.007
21.2	20.6	16.8	68.4	6.36	0.194	0.010	0.008
30.3	30.3	26.2	72.2	8.92	0.286	0.011	0.011
20.0	20.0	11.0	30.4	12.10	0.895	0.019	0.016
20.0	20.0	10.0	24.0	13.23	0.631	0.017	0.017
30.9	30.3	19.6	36.2	21.64	1.722	0.026	0.028
31.4	30.1	19.3	35.5	22.92	1.015	0.027	0.029
32.6	32.6	20.7	33.3	24.42	1.491	0.032	0.031
32.8	32.8	19.5	27.5	26.83	1.672	0.030	0.034

In order to secure sufficient clarification for polarizing a raw sugar it is frequently necessary to allow a portion, if not all the solution, to filter a second time. To find what portion of this total evaporation affects the solution which runs through and is used for polarization, tests were made on the saccharimeter. A tube was filled with the solution directly from the flask in which it was made up, thus obviating any loss by evaporation. Other solutions after being allowed to filter were polarized and compared to the first tube as a point of reference. The difference in polarization between this tube and the other tubes is the effect due to evaporation during filtration. Careful experiments by weighing failed to show an appreciable evaporation while pouring the solution from the cylinder into the tube. Tables 2 and 3 show the effect of evaporation upon the polarization when the funnel is not covered. The time of filtration was about 12 minutes. It was hoped that the equations from this data would give the correction factors which would be applicable to raw sugars. Table 2 shows the increase in polarization for a single filtration, and we have

$$\frac{Q}{T}=0.00066(P_s-P_a) \qquad (5)$$

Table 3 shows the increase when the entire solution is filtered twice, and we have

$$\frac{Q}{T}=0.00108(P_s-P_a) \qquad (6)$$

The results are shown graphically in Fig. 1. It is surprising to find such a large increase per minute in the polarization when the solution is filtered twice.

TABLE 2

Refined Sugar; Funnel not Covered; Determinations by Polarization; Filtered Once

$$\left[\frac{Q}{T}=0.00066\ (P_s-P_a)\right]$$

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 P_s-P_a, mm of Hg	6 Total change, degrees sugar	7 Observed $\frac{Q}{T}$, degrees sugar	8 Calculated $\frac{Q}{T}$, degrees sugar
°C	°C	°C	Per cent				
30.4	30.4	27.9	82.6	5.65	0.08	0.007	0.004
20.0	20.0	12.4	40.0	10.45	0.03	0.006	0.007
19.9	19.9	11.2	32.6	11.66	0.16	0.009	0.008
32.0	33.0	23.0	42.4	19.49	0.25	0.014	0.013
34.0	36.6	19.2	17.2	31.72	0.24	0.017	0.021
35.1	36.2	18.8	16.7	34.61	0.30	0.023	0.023
36.0	37.9	20.1	19.5	35.62	0.18	0.025	0.024

TABLE 3

Refined Sugar; Funnel not Covered; Determinations by Polarization; Filtered Twice

$$\left[\frac{Q}{T} = 0.00108\,(P_s - P_a)\right]$$

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 $P_s - P_a$, mm of Hg	6 Total change, degrees sugar	7 Observed $\frac{Q}{T}$, degrees sugar	8 Calculated $\frac{Q}{T}$, degrees sugar
°C	°C	°C	Per cent				
30.4	30.4	27.9	82.6	5.65	0.11	0.003	0.006
20.0	20.0	12.4	40.0	10.45	0.22	0.011	0.011
19.9	19.9	11.2	32.6	11.66	0.35	0.013	0.013
32.0	33.0	23.0	42.4	19.49	0.43	0.019	0.021
35.1	36.2	18.8	16.7	34.61	0.50	0.038	0.037

Since equations (4), (5), and (6) show such large increases in the polarization, the experiments given in Tables 1 and 2 were repeated with the funnels covered with ordinary cover glasses, in order to determine how completely the evaporation could be prevented by this simple expedient. The results are given in Tables 4 and 5. In Table 4 the values in column 8 are calculated from equation (4) and in Table 5 from equation (6).

TABLE 4

Refined Sugar; Funnel Covered; Determinations by Weighing

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 $P_s - P_a$, mm of Hg.	6 Total change	7 Observed $\frac{Q}{T}$, grams per minute	8 Calculated $\frac{Q}{T}$, grams per minute if not covered
°C	°C	°C	Per cent		g		
21.1	20.8	17.4	71.8	5.50	0.028	0.001	0.007
30.0	30.0	26.0	72.8	8.57	0.052	0.001	0.011
20.0	20.0	11.0	30.4	12.10	0.031	0.001	0.016
20.0	20.0	10.0	24.0	13.23	0.060	0.001	0.017
30.9	30.3	19.6	36.2	21.64	0.062	0.001	0.028
31.4	30.1	19.3	35.5	22.92	0.047	0.002	0.029
32.8	32.8	19.5	27.5	26.83	0.035	0.001	0.034

TABLE 5

Refined Sugar; Funnel Covered; Determinations made by Polarization; Filtered Twice

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 P_s-P_a, mm of Hg.	6 Total change, degrees sugar	7 Observed $\frac{Q}{T}$, degrees sugar.	8 Calculated $\frac{Q}{T}$, if not covered, degrees sugar.
° C	° C	° C	Per cent				
20.0	20.0	12.4	40.0	10.45	0.00	0.000	0.007
20.0	20.0	10.2	25.3	13.01	0.02	0.001	0.014
20.0	20.0	10.2	25.3	13.01	0.06	0.002	0.014
20.0	20.0	10.2	25.3	13.01	0.03	0.000	0.014
20.0	20.0	10.2	25.3	13.01	0.03	0.001	0.014

It is evident from Tables 4 and 5 that the loss by evaporation, if the funnel is covered, is quite negligible, for all potential heads, amounting to only 0°.02 S for a filtration requiring 20 minutes. The object of the latter table was mainly to determine the agreement between the weighing and polarization methods. Four separate experiments were made at a potential head of 13 mm, in order to test the reproducibility of the polarization method.

EXPERIMENTS WITH RAW SUGAR

The experiments on refined sugar indicated the importance of making exhaustive tests on different grades of raw sugars to determine how far the preceding results could be applied to sugars requiring clarification. Three grades were used: Java, testing 97° S; Cuban, testing 94° to 95° S; and a very soft sugar, testing about 80° S. No appreciable differences in the evaporation were observed due to the grade of sugar. In every case 260 g was dissolved in water and the volume made up to 1000 cc at the temperature of the experiment. From 15 cc to 50 cc of basic lead acetate was added for clarification, the quantity used varying with the grade of sugar; 100-cc portions of the liquid were then used for the tests. The flask was thoroughly shaken before pouring off each portion, thus insuring a homogenous sample. To obtain a point of reference one filtration was always made with the funnel covered. The change by evaporation from this sample was not greater than 0.02° S, as has been shown in Tables 4 and 5. Other portions of the solution were filtered without being covered and were compared to the reference tube. The results are given in Tables 6, 7, 8, and 9. The same method of tabulating the data has been used as in the tables for refined sugars. Since no difference in $\frac{Q}{T}$ was observed, due to the grade of the sugar, the values obtained for the three different grades have been incorporated into a single equation.

For the experiments in Table 6, the solutions were filtered once with the funnels uncovered, and we find

$$\frac{Q}{T} = 0.00017(P_s - P_a) \tag{7}$$

The results are shown graphically in Fig. 2.

TABLE 6

Raw Sugar; Funnel not Covered; Determinations by Polarization; Filtered Once

$$\left[\frac{Q}{T} = 0.00017(P_s - P_a)\right]$$

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 $P_s - P_a$, mm of Hg	6 Total change, degrees sugar	7 Observed $\frac{Q}{T}$, degrees sugar	8 Calculated $\frac{Q}{T}$, degrees sugar
°C	°C	°C	Per cent				
27.8	28.0	25.3	80.0	4.21	0.02	0.001	0.001
27.5	27.6	24.8	79.8	5.42	0.04	0.002	0.001
24.1	24.1	14.0	30.9	15.42	0.12	0.005	0.003
24.8	24.8	14.1	28.4	16.66	0.03	0.003	0.003
25.0	25.1	13.9	26.5	17.29	0.06	0.006	0.003
28.4	27.3	15.8	28.2	21.18	0.02	0.001	0.004
30.4	27.3	15.8	28.2	24.70	0.11	0.005	0.004
34.0	36.9	19.2	16.5	31.92	0.10	0.006	0.006
37.4	39.0	20.7	17.2	38.79	0.05	0.004	0.007
38.4	39.1	20.9	17.8	41.16	0.08	0.007	0.007
38.4	39.1	20.9	17.8	41.16	0.11	0.008	0.007

For Table 7 the solutions were poured back when one-half had filtered. The funnels were not covered. We then have—

$$\frac{Q}{T}=0.00049(P_s-P_a) \qquad 8$$

The results are shown graphically in Fig. 2.

TABLE 7

Raw Sugar; Funnel not Covered; Determination by Polarization; Solution Poured Back When One-Half Filtered

$$\left[\frac{Q}{T}=0.00049(P_s-P_a)\right]$$

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 P_s-P_a, mm of Hg	6 Total change, degrees sugar	7 Observed $\frac{Q}{T}$, degrees sugar	8 Calculated $\frac{Q}{T}$, degrees sugar
°C	°C	°C	Per cent				
27.8	28.0	25.3	80.0	4.21	0.05	0.002	0.002
27.5	27.6	24.8	79.8	5.42	0.03	0.001	0.003
24.6	24.6	14.8	33.0	15.32	0.20	0.005	0.007
24.8	24.8	14.1	28.4	16.66	0.22	0.011	0.008
25.0	25.1	13.9	26.5	17.29	0.25	0.013	0.008
28.4	27.3	15.8	28.2	21.18	0.22	0.010	0.010
30.4	27.3	15.8	28.2	24.70	0.46	0.013	0.012
34.0	36.9	19.2	16.5	31.92	0.62	0.023	0.016
37.4	39.0	20.7	17.2	38.79	0.23	0.012	0.019
38.4	39.1	20.9	17.8	41.16	0.30	0.022	0.020
38.4	39.1	20.9	17.8	41.16	0.34	0.017	0.020

For Table 8 the solutions were filtered twice with the funnels uncovered. We have—

$$\frac{Q}{T}=0.00070(P_s-P_a) \qquad 9$$

The results are shown graphically in Fig. 2.

TABLE 8

Raw Sugar; Funnel not Covered; Determination by Polarization; Filtered Twice

$$\left[\frac{Q}{T} = 0.00070(P_s - P_a)\right]$$

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 P_s-P_a, mm of Hg	6 Total change, degrees sugar	7 Observed $\frac{Q}{T}$, degrees sugar	8 Calculated $\frac{Q}{T}$, degrees sugar
°C	°C	°C	Per cent				
27.8	28.0	25.3	80.0	4.21	0.17	0.005	0.003
27.5	27.6	24.8	79.8	5.42	0.20	0.005	0.004
24.1	24.1	14.0	30.9	15.42	0.45	0.011	0.011
28.4	27.3	15.8	28.2	21.18	0.55	0.016	0.015
30.4	27.3	15.8	28.2	24.70	0.84	0.018	0.017
34.0	36.9	19.2	16.5	31.92	1.16	0.023	0.022
37.4	39.0	20.7	17.2	38.79	0.78	0.026	0.027
38.4	39.1	20.9	17.8	41.16	0.78	0.029	0.029
38.4	39.1	20.9	17.8	41.16	0.68	0.023	0.029

In Table 9 the funnels were covered. A point of reference was secured by allowing a sample to filter once, since it was impossible to polarize without filtration. For the other tests the solution was poured back on the filter when (*a*) about one-half had run through; (*b*) all had run through. The cover was removed from the funnel while the solution was being poured back and was then immediately replaced.

Column 8 was calculated from equations (8) and (9).

TABLE 9

Raw Sugars; Funnels Covered; Determination by Polarization.

1 Temperature of body of solution	2 Dry-bulb temperature	3 Wet-bulb temperature	4 Relative humidity	5 P_s-P_a, mm of Hg	6 Total change, degrees sugar	7 Observed $\frac{Q}{T}$, degrees sugar	8 Calculated $\frac{Q}{T}$ if not covered, degrees sugar
°C	°C	°C	Per cent				
24.6	24.6	14.8	33.0	15.32	0.000	0.000	[4]0.008
24.6	24.6	14.8	33.0	15.32	0.015	0.001	[4]0.008
24.6	24.6	14.8	33.0	15.32	−0.025	−0.001	[5]+0.010
24.6	24.6	14.8	33.0	15.32	0.020	0.001	[5]0.010

[4] Poured back when half through.

[5] Poured back when all through.

DISCUSSION OF RESULTS

In the preceding experiments $\frac{Q}{T}$ has been measured for potential heads as high as 41 mm of mercury. During the summer months, when it is most likely to be a maximum, the potential head rarely exceeds 22 mm and is usually much lower; 22 mm corresponds roughly to a temperature of 30° and a relative humidity of 30 per cent. $\frac{Q}{T}$ for the curve obtained by weighing is much larger than the corresponding value obtained by the polarization method. (See Fig. 1.) This probably is caused by the evaporation from the solution that remains on the filter and which produces no increase in the concentration of the solution which passes the filter. The method of weighing determines the total evaporation, whereas not all the evaporation is instrumental in raising the polarization when that method is utilized.

The curves in Fig. 2 show at a glance how inapplicable the conrections for refined sugar are to raw sugars. $\frac{Q}{T}$ for the once filtered solution is suprisingly small when compared with the similar curve in Fig. 1. Certainly evaporation from a solution containing a precipitate is much slower than from one containing none. We believe that this phenomenon, because of its direct effects on many laboratory operations, should receive further study.

When the solution is filtered but once, the increase in the polarization (see Fig. 2) for a potential head of 22 mm and a filtration of 10 minutes duration, is less than 0°.04 S. The conclusion, therefore, is reached that it is unnecessary, in the ordinary testing of raw sugars, to use any precautions to prevent or to correct for evaporation, provided that it is not necessary to pour any portion of the filtrate back on the filter. All the more unexpected, then, is the large increase in $\frac{Q}{T}$, as shown by the curves in Fig. 2, when a part or all of the solution is filtered a second time. After careful consideration we have concluded that this is caused largely by the solution which is returned to the filter taking up the solution

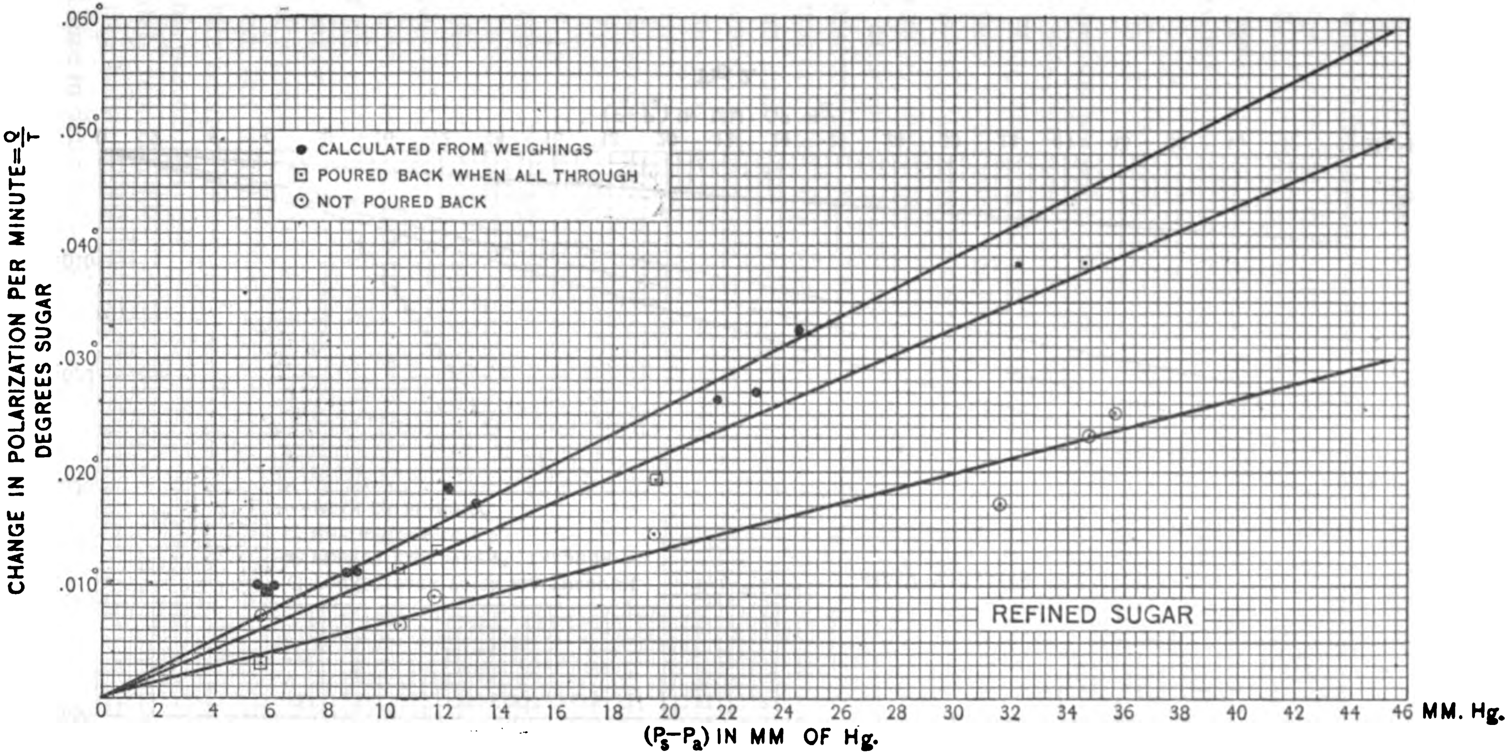
CHANGE IN POLARIZATION PER MINUTE=$\frac{Q}{T}$ DEGREES SUGAR
.060°
.050°
.040°
.030°
.020°
.010°
● CALCULATED FROM WEIGHINGS
⊡ POURED BACK WHEN ALL THROUGH
⊙ NOT POURED BACK
REFINED SUGAR
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
MM. Hg.
(P_s–P_a) IN MM OF Hg.

Fig. 1.

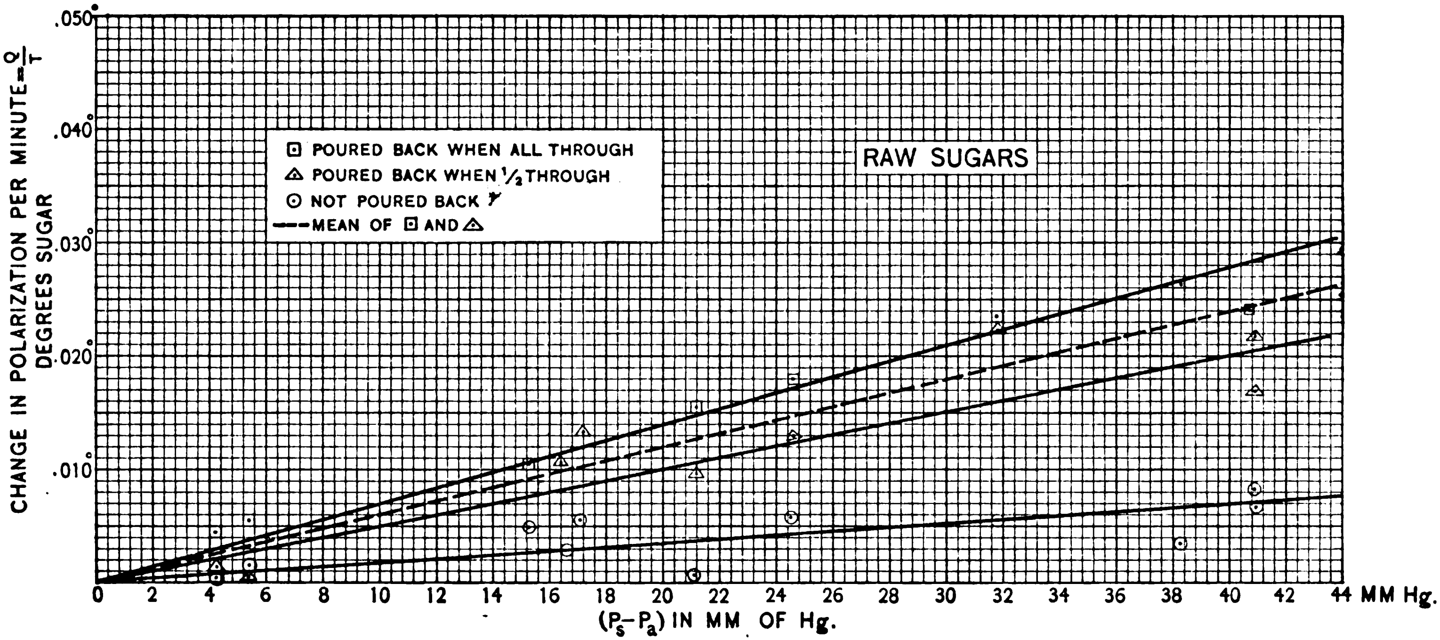
RAW SUGARS
⊡ POURED BACK WHEN ALL THROUGH
△ POURED BACK WHEN 1/2 THROUGH
⊙ NOT POURED BACK
---MEAN OF ⊡ AND △
CHANGE IN POLARIZATION PER MINUTE = Q/T DEGREES SUGAR
.050°
.040°
.030°
.020°
.010°
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44 MM Hg.
(P_s−P_a) IN MM OF Hg.

Fig. 2.

already adhering to the filter and which has become concentrated by evaporation after the level of the solution in the funnel has fallen. It thus becomes imperative in this case either to prevent evaporation or to apply a correction to the polarization. The correction may most conveniently be taken from the broken curve $\frac{Q}{T} = 0.00060\ (P_s - P_a)$, which is the mean of the curve for solutions poured back when one-half has filtered, and the curve for solutions twice filtered. (See Fig. 2.)

Since the practice of returning at least a part of the first filtrate to an uncovered filter is quite general, the conclusion is unavoidable that in many laboratories tests are frequently in error by several tenths of a sugar degree. The important influence of atmospheric conditions on sugar tests has remained so long undetermined, probably because polarizations made on the same sugar and compared with one another are usually made at the same time and hence under similar potential heads. The results, therefore, agree among themselves, although relatively large errors may be present. The importance of either eliminating or correcting for the evaporation when tests made in different laboratories are to be compared can not be overestimated.

Tables 4, 5, and 9 show that for most purposes any increase in the polarization may effectively be prevented by covering the funnel during the filtration. In laboratories where a large number of tests are made daily this is somewhat of a burden, but it is generally a simpler procedure than making the correction for the potential head.

Owing to the importance, for scientific and commercial purposes, of the 100° S point on the saccharimeter, it is desirable that this point be determined with the highest obtainable precision. Especially prepared sucrose is used, and the solution is not only unfiltered, but it is also protected from any change in concentration while being transferred from the flask to the polarization tube. This procedure is necessary in order to obtain a result that is accurately reproducible. It is surprising that in view of the dissimilarity between the method for testing raw sugars and the procedure in determining the 100° S point that the effects of changes in concentration have not been carefully studied. It has long been recognized that the ideal conditions of having both procedures identical is not practicable. The possibility of errors has always been admitted, but owing to the lack of accurate data on the subject the matter has been generally ignored. Unfortunately, the uncertainty thus introduced has been used at times as an argument against a revision of the 100° S point, the statement being made that it was not necessary to know the 100° S point accurately, because of the possible errors in the polarization of a sugar, due to changes in concentration. The results of the present investigation would seem to eliminate from consideration this argument against an accurate revision of the 100° S point of the saccharimeter.

As a result of the conclusions which have been drawn from the preceding data we would suggest the following for the guidance of those who desire to secure the true polarizations of raw sugars:

RAW SUGAR, FILTERED ONCE

1. The increase in the polarization due to evaporation is negligible in ordinary testing for all potential heads up to 22 mm and it is therefore unnecessary to use any precautions to prevent or to correct for evaporation for ordinary atmospheric conditions, provided the duration of the filtration does not exceed 10 or 12 minutes.

2. If the correction for the increase in polarization is desired, it may be obtained from

$$Q = 0.00017\ (P_s - P_a)\ T \qquad (10)$$

where Q = increase in polarization in degrees sugar.

P_s = saturation vapor pressure at the temperature of the solution.

P_a = saturation vapor pressure at the temperature of the dew point in the air.

T = time of filtration, in minutes.

Q should be subtracted from the observed polarization to obtain the true polarization.

3. Practically all increase in polarization, regardless of atmospheric conditions, may be prevented by covering the funnel with a watch glass.

RAW SUGAR; NOT LESS THAN ONE-FOURTH OF SOLUTION FILTERED TWICE

4. The increase in the polarization due to evaporation is not negligible in ordinary testing, but may amount to several tenths of a sugar degree. It is therefore necessary to prevent or to correct for evaporation for ordinary atmospheric conditions.

5. The correction for the increase in the polarization may be calculated from

$$Q = 0.00060\ (P_s - P_a)\ T \qquad (11)$$

where Q, P_s, P_a, and T have the definitions given in 2. Q should be subtracted from the observed polarization to obtain the true polarization.

6. Practically all increase in polarization, regardless of atmospheric conditions, may be prevented by covering the funnel with a watch glass.

WASHINGTON, February 1, 1914.

FLAME STANDARDS IN PHOTOMETRY[1]

By E. B. Rosa and E. C. Crittenden

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I. INTRODUCTION

1. PRESENT PRIMARY STANDARDS OF LIGHT

The need of a reliable standard to serve as a basis for the measurement of light has long been recognized, and in attempts to meet this need much ingenuity has been applied and a tremendous amount of labor has been expended. No standard yet produced has, however, shown such evident superiority as to obtain general acceptance. In France, Germany, and England different forms of flame standards have been recognized as primary standards, but no one of them has been considered entirely satisfactory.

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[1] This paper is a revision of one published in the Transactions of the Illuminating Engineering Society (Vol. 5, pp. 753–778; 1910), under the title "Report of progress on flame standards." More recent developments have not materially changed the conclusions then stated, and the present paper differs from the original in form more than in substance. Many additional measurements have been made, covering in all about 80 pentane lamps, but so far as the purposes of this paper are concerned the older data show the performance of the lamps as well as the newer results would, and with a few exceptions the original tables have been retained.

In France the Carcel lamp, invented about 1800, was raised to the dignity of a standard largely as a result of its use as a convenient comparison lamp by Fresnel, although definite directions for its use were not published until 1862, and even those directions have had to be radically modified in recent years.[2] The later prestige of the lamp arose from the fact that Violle practically defined his unit in terms of the Carcel, and in default of a reproduction of the Violle platinum standard, the French unit (the bougie décimale) adopted by the International Electrical Congress of 1889, was in practice maintained by the Carcel lamp, the candlepower of which was taken as 9.62 bougies décimales.

The Hefner lamp was proposed by von Hefner-Alteneck in 1884 and rapidly displaced the candles previously used in Germany. In 1893 the Physikalisch-Technische Reichsanstalt began to certify lamps of this type, and in 1895 the present German unit, called at first the Hefnerlicht and later the Hefnerkerze, was defined as the intensity of a Hefner lamp under certain atmospheric conditions.

The Harcourt 10-cp pentane lamp, the final product of a series of pentane lamps devised by Vernon Harcourt and others, was adopted in 1898 for all tests made under the direction of the Metropolitan Gas Referees of London. Since some doubt existed regarding the reproducibility of the lamps, the Engineering Standards Committee defined its unit of candlepower as one-tenth of the candlepower under standard conditions of a particular lamp kept at the National Physical Laboratory.

The defects of such standards are illustrated by the fact that for years after the three types were adopted in the respective countries there remained a considerable margin of uncertainty as to the relative numerical values of the three units. Several direct intercomparisons of the flame standards gave more or less discordant results, and no definite agreement was reached until a comparison of the units actually used in each of the national standardizing laboratories was obtained through measurements of groups of seasoned electric incandescent lamps carried from one laboratory to another. These measurements showed that within the limits of experimental error the units in use in France and in

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[2] J. Gas Lighting, 99, p. 234; 1907.

England were equal, while the Hefnerkerze was 0.9 as large as the others; and this simplicity of ratios made possible the agreement which has reduced the units of light to two, namely, the Hefnerkerze and the international candle of England, France, and America.[3]

The light unit of the Bureau of Standards has always been maintained by groups of electric lamps, because it has been believed that the unit once agreed upon could be so maintained with an accuracy considerably above that with which it could be reproduced by reference to any of the so-called reproducible standards at present in use. In other words, the incandescent lamps have really been employed as primary standards, and the flame standards, which logically should play the part of primary standards, have been relegated to a subordinate position. For example, a given pentane lamp is not assumed to give 10 candles, but is compared with the electric standards and is assigned a value as a result of the comparison.

2. NEED OF A BETTER STANDARD

Although the electric lamps are very satisfactory as secondary standards, and although as empirical primary standards they may serve to maintain the unit of light constant for many years, yet there is a possibility of an appreciable drift in the value of the unit occurring sooner or later, if there is no photometric standard accurately reproducible from its specifications which is capable of serving as a reliable check upon the electric standards. Consequently, while the present unit may be considered as definitely and permanently adopted, there is need of a reproducible standard to preserve the value of that unit unchanged. There have been proposed several possible methods of constructing such standards which would be more rational than the essentially crude flame standards, but not one of them has yet been developed to a sufficient extent to be of any use as a permanent custodian of the unit, and none gives much promise of being able to supplant the flame lamps in the immediate future. It has therefore appeared worth while to make a study of the best types of flame lamps to see how closely they would reproduce in our laboratory the values adopted by international agreement and also to find whether their reliability as primary standards could be increased by any changes in construction or in operation.

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[3] Circular of the Bureau of Standards, No. 15, on the "International unit of light."

Another reason for improving flame standards is their extensive use in gas photometry, to which they are in some respects better adapted than electric standards. At the suggestion of representatives of the gas industry, the Bureau of Standards some years ago took up the study of some of the more important flame standards with the hope of improving current practice in gas testing in American cities. We may anticipate our conclusion by saying that for such use the pentane lamp has appeared far superior to any of the others, and the results of the Bureau's experience have been incorporated in a special paper[4] for the guidance of those who may have occasion to use that form of lamp.

The present paper is intended to give some of the details of the experimental work done on lamps of various types which have found a more or less extensive use. The most important are the three primary flame standards mentioned above, and the modified form of the pentane lamp which is widely used in the United States, and only these four forms will be considered.

In any flame standard the lamp itself is not the standard but, along with the fuel and the air, it constitutes a means for producing the actual standard, the flame. In considering the property of reproducibility we have therefore to interpret the word in a double sense; we must consider the possibility of producing different lamps and different lots of fuel which are sufficiently like each other to give sensibly the same candlepower, and we must also take into account the exactness with which a given lamp can be made to reproduce the intensity of its flame at different times. In a secondary standard the second consideration is the one of chief importance. In a primary standard a high degree of reproducibility of this second kind is desirable but is not really indispensable, provided the departures from normal value are not systematic; the property of first importance is the reproducibility of the lamp and the fuel.

The excellent performance of the electric lamps makes it possible to test very accurately the qualities of various lamps, for we can not only measure the lamps from day to day and compare various lamps with each other with the certainty that the basis of comparison remains constant, but we can also determine whether lamps of each type give the same intensity as is found in other laboratories, and hence can form an opinion as to the possibility of an independent reproduction of the unit.

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[4] The Pentane Lamp as a Working Standard, this Bulletin, **10**, pp. 391–415; 1913.

II. EFFECTS OF ATMOSPHERIC CONDITIONS

1. VARIATIONS IN THE ATMOSPHERE

Besides the lamp and the fuel the third factor, the air, must be considered, for it affects the intensity of the flame very markedly. Oxygen is supplied by the atmospheric air drawn into the flame. With the oxygen go nitrogen, carbon dioxide, and water vapor, which are not needed for combustion and which cool the flame and reduce its intensity. If the air supplied to the flame varies in its composition, the rate of combustion is altered and the cooling effect of the inert gases varies. Fortunately the proportions of oxygen, nitrogen, and carbon dioxide in the open air are remarkably constant and are sensibly the same in different places, so that it is not difficult to obtain standard conditions in this respect if the photometer room has provision for a liberal continuous supply of fresh air. In the present work therefore no attempt has been made to determine the effects of abnormal quantities of carbon dioxide or of a deficiency of oxygen, but care has been taken to secure such good ventilation that no correction would be necessary for such variations in the composition of the air.

The barometric pressure and the proportion of water vapor in the air are, however, variable, and it is not easy to control the variations so as to obtain normal conditions. Consequently, in order to determine the normal value of a flame standard, it is usually necessary to apply corrections for the departure of these two conditions from normal.

The necessary correction factors, the rates of change of candlepower with variation in barometric pressure and in atmospheric moisture, have been previously determined for both the Hefner and the pentane lamp, but the determinations have not agreed as well as they should. The discrepancy between the results obtained at the Physikalisch-Technische Reichsanstalt and those of the English National Physical Laboratory is great enough to cause a difference of over 1.5 per cent in the average corrected value of lamps measured at Washington in the summer. The data of the present investigation are sufficient to give a new determination of those factors, and with respect to the effects of water vapor the results have been so definite and consistent that the new value has been adopted for use both in reducing the data presented in this paper and in calculating the normal values of lamps tested at the Bureau.

2. EFFECT OF BAROMETRIC PRESSURE

The range of barometric pressure included in these measurements has not been sufficient to give a thoroughly reliable value for the corresponding correction factor, and the results have been considered only as an approximate check on previous values. In Table 1 are given the results obtained by various investigators:

TABLE 1

Percentage Decrease in Candlepower Caused by a Fall of 1 cm in Barometric Pressure

Authority	Hefner lamp	10-cp pentane lamp
Liebenthal[5]	0.11	0.6
Paterson[6]	.2	.8
Butterfield, Haldane & Trotter[7]	.4	.8
Bureau of Standards	.14	0.6–0.8

[5] Zs. f. Instrument., **15**, p. 163, 1895; J. f. Gas. u. Wasser., **49**, p. 561, 1906.

[6] Electrician (London), **53**, p. 751, 1904; J. Institution of Elect. Eng., **38**, p. 271, 1906–7; J. Gas Light., **99**, p. 232, 1907; N. P. L., Collected Researches, **8**, p. 49, 1908.

[7] J. Gas Light., **115**, p. 290, 1911; Amer. Gas Light J., **95**, p. 145, 1911.

The Bureau's earlier measurements, of which the results were published in 1910, gave an average value of 0.6 per cent for the factor for the pentane lamp, but since the range of pressures was very small the value 0.8 per cent, which seemed better established, has been used in correcting observations on test lamps. Later measurements with slightly greater range continued to give somewhat discordant results, until our most recent experiments which tend to confirm the value 0.6 at normal atmospheric pressure. It may be noted from the table that the pentane lamp is affected decidedly more than the Hefner by variation in pressure, and there is evidence that on some flames the effect is still greater. Since for some purposes this effect and the relative change in various types of flame are important, there has recently been undertaken at this Bureau a special investigation of this subject, in which the determination of the effect on the flame standards over considerable ranges of pressure is being made. Within the range of pressure which occurs at Washington the present uncertainty in the correction factor is not of great importance, since the possible errors introduced by it are within the errors of measurement.

3. EFFECT OF WATER VAPOR

The discrepancies between the different values previously given for the water-vapor correction factor are much more serious, and it is therefore a source of gratification that the determinations at the Bureau have been remarkably consistent over the period of four years during which this work has been carried on.

The first thorough investigation of the effect of atmospheric moisture on flames was made by Liebenthal at the Physikalisch-Technische Reichsanstalt, and the method of expressing the variation used by him has been generally followed by others. The humidity (h) is stated in liters of water vapor per cubic meter of (dry) air, and it is found that the variation in intensity of flames is proportional to the humidity. Consequently, if the candlepower of a lamp is defined as normal (I_n) when there are n liters of water vapor per cubic meter of air, the candlepower (I) corresponding to any proportion of water vapor is given by the equation

$$I = I_n[1 + a(n-h)]$$

The method of determining the humidity is to ascertain, by means of a hygrometer, the pressure of the water vapor in the atmosphere at the time of the measurements. This divided by the barometric pressure minus the vapor pressure gives the ratio of the water vapor to the dry air with which it is mixed; this ratio multiplied by 1000 gives the number of liters of water vapor in 1000 of dry air; that is, in a cubic meter of dry air. For other purposes it is more common to state the number of liters of water vapor in a cubic meter of the damp atmosphere. The difference between the two methods of calculation is negligible except at extremely high humidities, but in order to make the results exactly comparable with those of other investigators, the calculations in this paper are based on dry air.

It is evident that the adoption of a flame lamp as a primary standard does not fix the value of the unit unless a standard humidity is specified. The normal humidity for the Hefner lamp has been fixed as 8.8, this being the condition under which Liebenthal found the lamp to give the intensity which had already been adopted as the unit of the Reichsanstalt. For the pentane lamp the normal humidity was originally given as 10 liters per cubic meter of air, which was the average humidity shown by the observations of three years at the Meteorological Office in London and the National Physical Laboratory Observatory at Kew. It later developed that in the calculation of the results of observations on the lamp an error had been made, and that the condition which had been taken as normal was not actually a humidity of 10 liters per cubic meter. Atmospheric humidities were formerly measured at the National Laboratory (as generally in England) by the ordinary wet and dry bulb thermometers, without any artificial ventilation, while in the other countries the instrument used was the more accurate hygrometer (psychrometer) of Assmann, which is ventilated by a rapid current of air and which, therefore, gives a greater depression of the wet bulb. The unventilated hygrometer gives fairly correct results if one uses the tables or formula appropriate to that instrument, although it is less reliable, owing to the fact that the air in the room is not always equally still. It appears, however, that the formula used at the National Physical Laboratory was the formula for the ventilated hygrometer, and hence the values of the humidity obtained were too high.

When this error was discovered, there were two ways of correcting it. The number 10 might have been retained as giving the normal humidity, but since the actual humidity which had been called normal was less than 10 liters per cubic meter of air, raising the normal to an actual 10 liters would be equivalent to decreasing the normal intensity of the lamp. Retaining the 10 would therefore make it necessary either to reduce the unit of candlepower slightly or to assign for the normal intensity of the standard pentane lamp a value somewhat below 10 candles. The other method of adjustment was to leave unchanged all the actual quantities (humidity, unit of candlepower, and candlepower of the standard lamp), and to put into the formula instead of 10 the number which correctly represented the humidity previously given as 10 liters per cubic meter of air. This appeared to be the most reasonable method of effecting the correction. Moreover, it would retain the extremely simple ratios which had been found to exist between the French, English, and German units as maintained at the respective national laboratories.[8] This method was therefore adopted and Dr. Glazebrook announced in a paper read before the British association[9] that the humidity previously determined as 10 liters by the unventilated instrument was found to be actually 8, so that the correction formula was

$$\text{Candlepower} = 10 + 0.066\,(8 - h)$$

where h is the number of liters of water vapor in a cubic meter of dry air. The Gas Referees of London concurred in this proposal, and the official value of the pentane lamp has since been expressed by the above equation.

In effect, then, it is true of both the Hefner and the pentane lamps that a value approximating the yearly average was found by comparing the flame with electric lamps, and this average value, maintained by means of the electric standards, constituted the real unit of candlepower. Later the conditions under which the flame lamps themselves gave the standard values were determined, giving a more exact definition of the unit in terms of the flames.

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[8] The statement has been repeatedly made (see, for example, H. Krüss, J. f. Gasbeleuchtung, **52**, p. 705, 1909; J. Gas Lighting, **107**, p. 439, 1909; Amer. Gas Light J., **91**, p. 676, 1909; and the report of the German committee of the International Electrotechnical Commission, Elektrotech. Zeitschrift, **30**, p. 593, 1909) that the British candle was changed to secure this agreement, whereas in fact the course chosen was that which avoided a change in the unit of the National Physical Laboratory, which had been adopted by the Engineering Standards Committee as the British unit. Even in England there seems to have been an impression that the standard conditions were changed (see Electrician, **63**, p. 203, 1909), and this impression has found its way into various American publications. Unfortunately, in the numerous direct comparisons between flame standards which were made in 1906 and 1907 confusion arose from the different methods of measuring humidity, and the results obtained were not the real ratios between the units in use in the different countries. For instance, on the Continent measurements on the pentane lamp were reduced to a basis of 10 (actual) liters of water vapor per cubic meter of air, and consequently a low value was found for the pentane candle. In England, on the other hand, the value assigned to the Hefner was that obtained with a real humidity in the neighborhood of 7 instead of 8.8, and consequently Paterson found the large value 0.914 for the Hefnerkerze in terms of the unit of the National Physical Laboratory. Later, when proper corrections were made so that each standard was reduced to the normal condition obtaining in the laboratory where it constituted the primary standard, it was found that the direct comparisons gave results in close agreement with those obtained by interchanging electric standards. (See Paterson on "The Proposed International Unit of Candlepower," Phil. Mag. (6), **18**, p. 263, 1909; Proc. Phys. Soc. of London, **21**, p. 867, 1910; N. P. L. Coll. Researches, **6**, p. 117, 1910; J. Gas Lighting, **107**, p. 383, 1909.)

[9] B. A. Report, 1908, p. 623, and Electrician, **61**, pp. 922–923, 1908.

4. THE WATER-VAPOR COEFFICIENT

The choice of a normal humidity must of necessity be more or less arbitrary, but the value of the coefficient which gives the change in candlepower caused by a variation of one unit in the amount of water vapor is a matter for experimental determination. In Table 2 are given the values which have been published for this coefficient.

TABLE 2

Water-Vapor Correction Factors

[The numbers given are the percentage of decrease in candlepower caused by an increase of 1 liter of water vapor per cubic meter of air.]

Authority	Hefner lamp	10-cp pentane lamp
Liebenthal[10]	0.55	0.55
Paterson[11]	.66	.66
J. S. Dow[12]	....	.71
Butterfield, Haldane & Trotter[13]	.625	.625
Bureau of Standards	.56	.57

[10] See note 5, p. 562.

[11] See note 6, p. 562.

[12] Electrical Review (London), 59, p. 496; 1906.

[13] See note 7, p. 562.

The large value obtained by Mr. Dow is not entitled to much weight, because the measurements of humidity were made with an unventilated hygrometer and because the value given is apparently derived from 50 measurements of candlepower remaining after a half dozen others had been rejected on the ground that they differed by 2 per cent or more from the value to be expected.

It will be seen from the table that all investigators agree in the conclusion that the two kinds of lamps are affected equally by humidity; but observers disagree as to the magnitude of the effect. It appears therefore that the cause of the difference is probably to be found elsewhere than in the methods of operating the lamps. It is probable either that the methods of measuring the humidity are different or that some condition more or less systematically connected with the humidity, such as temperature or vitiation of the air, has affected measurements in some laboratories more than in others.

The accidental variation in the results obtained is not great even when relatively few measurements are made. For example, in Table 3, which shows the factors calculated separately from measurements made at the Bureau on six Hefner lamps, it will be seen that the "probable error" of the mean is small compared with the differences exhibited in Table 2.

TABLE 3

Water-Vapor Correction for Hefner Lamp

The factor given is the percentage of decrease in candlepower caused by an increase of 1 liter of water vapor per cubic meter of air.]

Lamp number	Number of measurements	Correction factor
786	19	0.525
887	20	0.564
1343	21	0.578
804	15	0.575
879	13	0.562
1342	13	0.532
Total........................	101	.....
Weighted mean............	...	0.557

Figs. 1 and 2 show the distribution of the observations on two typical lamps. The larger part of the measurements are grouped at low humidities, and consequently the slope of the curves depends very largely on a small number of observations at higher humidities. These observations were made under the conditions least favorable for accurate measurements, and the data of Table 3 might well be expected to show the extreme variations likely to arise from accidental errors of measurement. However, the values given for separate lamps in the table can hardly be considered as entirely independent determinations since the whole group of lamps were usually measured one after another in each set of measurements, and the agreement is therefore less significant than it would be if the measurements on the several lamps had been made at different times.

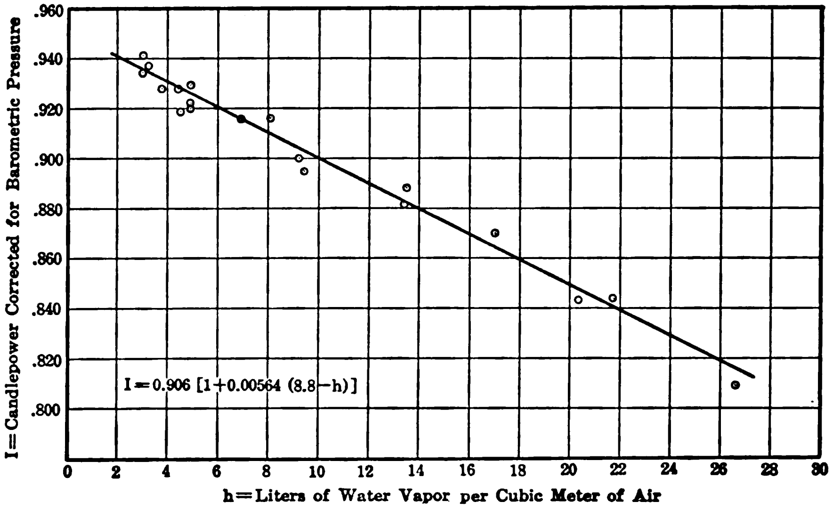

Fig. 1.—*Variation of candlepower with humidity, Hefner lamp No. 887.*

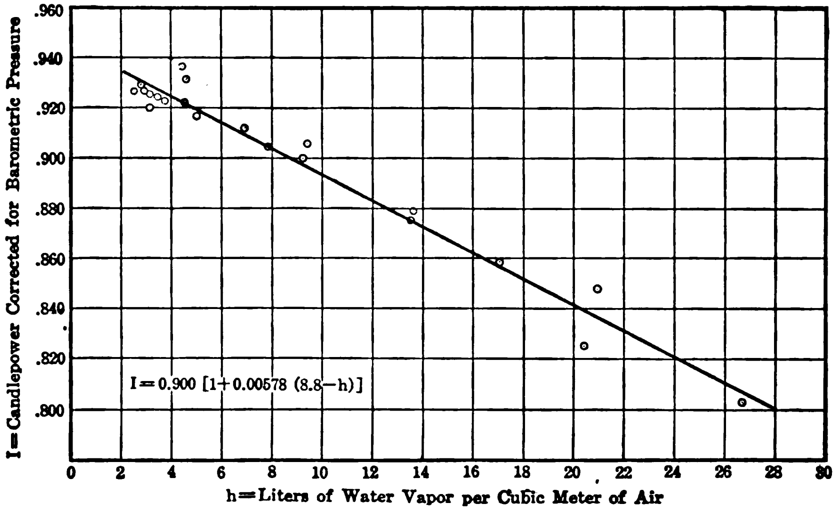

Fig. 2.—*Variation of candlepower with humidity, Hefner lamp No. 1343.*

On the pentane lamps many more measurements have been made, and the data obtained are sufficient for many entirely independent determinations of the correction factor. Table 4 gives the results published in 1910, and the observations on which these results were based are shown graphically in Figs. 3 and 4.

TABLE 4

Water-Vapor Correction for Pentane Lamps

[The factor given is the percentage of decrease in candlepower caused by an increase of 1 liter of water vapor per cubic meter of air.]

Lamp	Number of measurements	Factor derived	Range of water vapor (l per cu m of air)
Chance, No. 116	220	0.569	4.0–27.0
Chance, No. 118	81	0.572	14.1–26.8
Sugg, No. 171	165	0.561	4.0–27.0
Mean		0.567	
American, No. 25	42	0.577	5.0–14.3
American, No. 74	43	0.558	5.0–27.0
American, No. 157	46	0.570	18.2–26.8
American, No. 162	31	0.562	13.7–26.0
Total	628		
Mean		0.567	
Mean of all		0.567	

The same coefficient is found for the low range of humidities (4 to 14 liters per cubic meter) as for the higher range (14 to 27 liters per cubic meter); in other words, the relation between candlepower and humidity is linear from the lowest to the highest humidities encountered. The same coefficient is obtained for lamps of the American type as for those of the original form, and measurements made on the various lamps at different times as well as with different humidities agree very closely. The mean value, 0.567 per cent change in candlepower for a change of 1 liter per cubic meter in the water vapor, found from 628 observations on seven different lamps, would seem to be subject to very little uncertainty.

Since there seemed to be so little room for doubt that the smaller coefficient was correct, at least for the conditions encountered at the Bureau, an attempt was made to ascertain why the value found in England was so much higher. Mr. Paterson's work on the pentane lamp is of a high order and great confidence was placed in the precision of his measurements. It was recalled, however, as has been mentioned above, that in his experiments humidities had been measured with the ordinary unventilated hygrometer, whereas at the Bureau the Assmann instrument had always been used. In the paper announcing the change in the normal humidity, Dr. Glazebrook stated also that "a complete series of experiments has shown that the constant 0.066 in the formula holds both for the ventilated and unventilated instruments." This means, of course, that the constant is the same when the humidity is computed from observations made on unventilated hygrometers using the formula or tables intended for ventilated hygrometers, the only change in the correction formula being from 10 to 8 in the parenthesis. In other words, the straight line of which the correction formula is the equation has

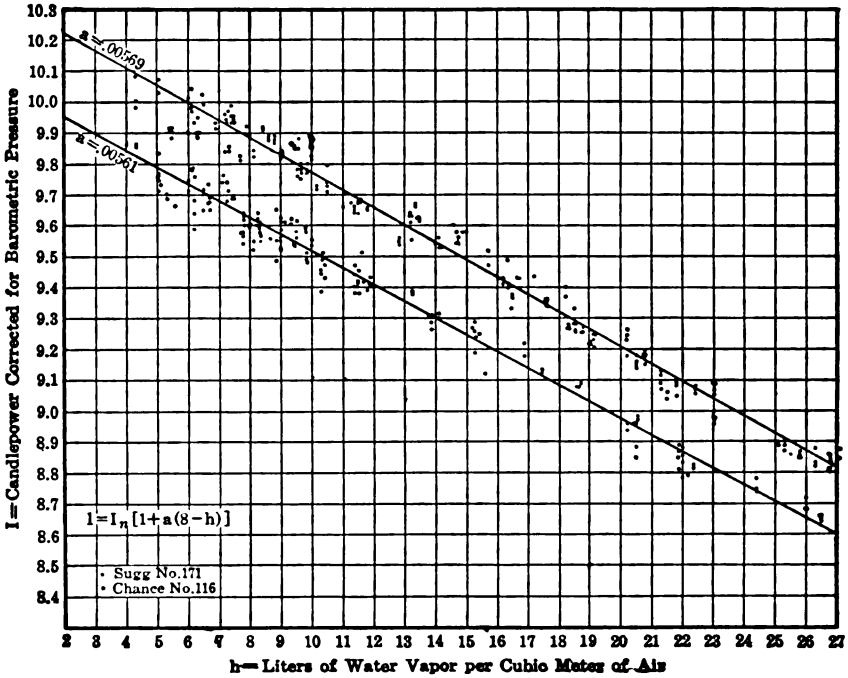

Fig. 3.—*Variation of candlepower of pentane lamps with humidity.*

been displaced parallel to itself, its slope remaining unchanged. A little consideration shows that this can only be true under special conditions.

In an unventilated hygrometer the air about the wet bulb retains some of the moisture taken up by the evaporation, and thus evaporation is retarded, whereas in the Assmann hygrometer the air moves over the bulb so rapidly that it is always surrounded with air of practically the same humidity as that of the room. Hence, the unventilated instrument will show a smaller depression than the other. The difference, which is considerable at low humidities, decreases as the humidity increases and disappears at saturation. That is, the depression of the reading of the wet-bulb thermometer is zero in both instruments in saturated air, and hence they will agree as to its humidity.

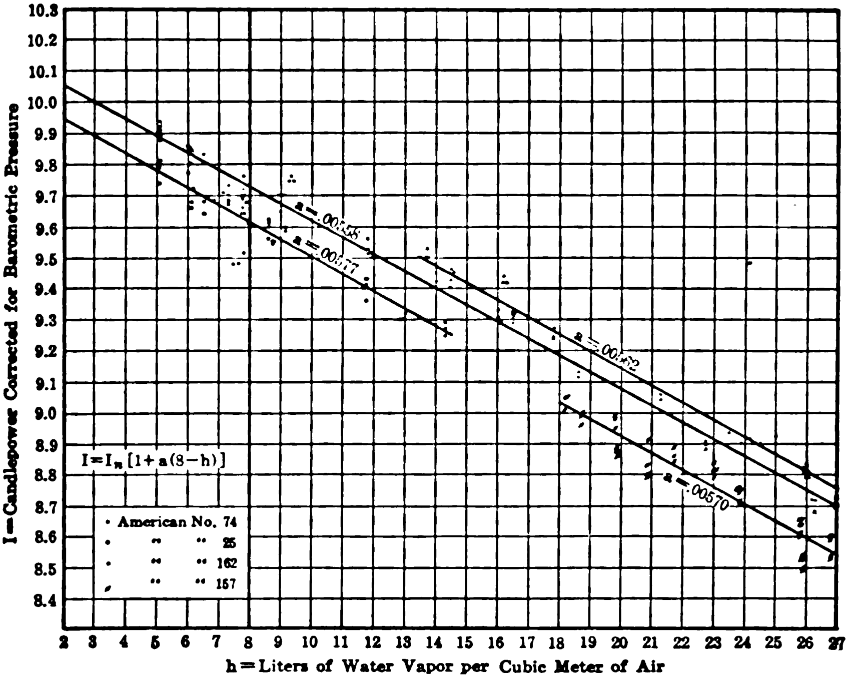

Fig. 4.—*Variation of candlepower of pentane lamps mith humidity.*

Suppose, for example, that a pentane lamp is measured in air that contains 8 liters of water vapor per cubic meter at 18° C, and again in air containing 20 liters of water vapor at the same temperature. Suppose its candlepower be found to be 10 international candles in the first case, and 9.32 candles in the second. The change of 0.68 candles is due to a change of 12 liters of water vapor per cubic meter, and since the change in candlepower is simply proportional to the humidity it is seen that the coefficient is 0.68 divided by 12, or 0.057. If, however, an unventilated hygrometer had been employed and an incorrect formula used, so that the first humidity came out 10 instead of 8, the second humidity would have been correctly shown to be full saturation, which the tables show to be 20 liters per cubic meter at 18° C, then the coefficient found would have been 0.68 divided by 10, or 0.068. This shows that there must be an error in the coefficient found if measurements at different humidities are made at the same temperature. If the higher humidities are at higher temperatures, as they generally are, the error will be less, and it is possible to choose temperatures and humidities so as to get the same error in the water vapor each time, and thus get a correct humidity coefficient.

In the weights and measures division of the Bureau of Standards, Mr. Pienkowsky has observed readings of an unventilated wet-and-dry bulb hygrometer and an Assmann ventilated hygrometer (both instruments in the same room) for several years past, calculating the humidities from both sets of observations. The expression for the difference between the pressure e_1 of saturated aqueous vapor at the temperature t_1 of the wet bulb and the actual vapor pressure e in the atmosphere is

$$e_1 - e = Ab\ (t - t_1),$$

where $t - t_1$ is the depression of the temperature of the wet bulb thermometer, b is the barometric pressure and A is a constant depending on the instrument and on the velocity of motion of the air over the wet bulb.

In Jelinek's tables for a mean barometric pressure of 755 mm the value of the product of Ab is taken as follows:

1. For still air	0.906
2. For slightly moving air	0.604
3. For rapidly moving air	0.495

The coefficient given for the Assmann hygrometer is 0.500. Mr. Pienkowsky has computed the humidity from the unventilated instrument, using the constant 0.906, and from the Assmann using 0.495, and the results have agreed as nearly as could be expected. When, however, the same formula is used for both instruments, the unventilated instrument, which gives smaller depressions of the wet bulb by from 0°.5 to 3° in actual practice, gives humidity values which are too high by from 1 to 4 liters of water vapor per cubic meter of air, the difference depending both on the absolute humidity and the temperature, being less as the humidity is greater, and less as the temperature is lower. It is, however, not the same at the same relative humidity, when both temperature and humidity vary. In order to ascertain what the average difference is between the two methods of obtaining humidity, some of Mr. Pienkowsky's observations have been used to compute the unventilated hygrometer readings by the formula for the other instrument, the differences being plotted against the actual humidities. The mean result is that 10 liters of water vapor per cubic meter of dry air by the unventilated instrument corresponds to 6 liters by the Assmann, under the conditions of temperature under which the observations were taken, namely, a temperature of about 20° C. If the laboratory temperature had been 15° C, the difference would have been about two liters. This conclusion has been checked by theoretical calculations from the formula using the coefficient 0.906 for the unventilated instrument, and 0.495 for the Assmann.

We have not learned what formulas were used by Mr. Paterson in determining his humidity coefficient and in recalculating the value on the basis of the ventilated hygrometer, but the data which he has kindly communicated to us seem to indicate that in his measurements the average relation between humidity and temperature was such as to make the error in the determination of the humidity practically constant and in the neighborhood of 2 liters.

Since the original publication of the Bureau's results, as given above, the work of Messrs. Butterfield, Haldane and Trotter has appeared, and correspondence with the National Physical Laboratory has failed to disclose any reason for the difference between our value and theirs. Consequently, our original data has been thoroughly examined for possible errors, and the results have been recalculated. In part of the original observations barometric pressures were taken from a barograph, checked at intervals. It was found that some small errors were introduced by this instrument, and in the recalculation correct pressure data furnished by W. C. Bishop have been used. The effect of these corrections, however, has been to leave the mean result absolutely unchanged, while the three lamps which were measured over the larger range of humidity are brought still closer to this mean. The coefficients derived for these three lamps become 0.568, 0.565, and 0.564, respectively. In terms of candlepower measurements, this agreement of results means that the curves derived give the same relative values for the three lamps at the lowest humidity as at the highest within less than one-tenth per cent.

Further determinations including some 2300 measurements on 27 different lamps in 1911 and 1912 have given identically the same result as the data of Table 4, and so far as accidental errors are concerned the value of the coefficient seems to be settled for the conditions under which measurements are made at the Bureau.

A possible explanation of the large differences between results obtained in different laboratories may be found in a direct effect of temperature on the candlepower. Changes of temperature and of humidity are closely related; the so-called humidity correction might really represent the combined effects of moisture and temperature changes. The relative variation of the two elements is probably not the same in different laboratories; for example, measurements made at the Bureau include a larger range of humidity than do those made at the National Physical Laboratory, while the range of indoor temperatures is probably about the same in the two laboratories, the average temperature at the Bureau being higher. We have not, however, been able to obtain any definite indication that changes of temperature within the usual laboratory range affect the candlepower of either the Hefner or the pentane lamp, and both Paterson and Butterfield, Haldane and Trotter have concluded that they do not affect the pentane lamp. It therefore appears unlikely that temperature effects will afford a solution of the difficulty.

It is perhaps worth noting that in case of insufficient ventilation there is a connection also between the humidity and the vitiation of the air, since the processes which exhaust the oxygen of the air usually produce considerable quantities of water vapor. If the arrangements are such that the thoroughness of the ventilation varies, there will be some tendency for the coincidence of high humidities with poor ventilation, for whenever the ventilation becomes insufficient the water vapor produced by the lamps and observers will increase the humidity. In a room where the flow of air depends on difference of temperature between indoor and outdoor air, still more serious effects might be produced by a systematic difference in the flow, which would probably be less in summer, and, if so, would tend to give fictitiously large values for the humidity effect. The room in which the present work has been done is supplied with air by a system of forced ventilation, assuring a flow independent of weather conditions. It was considered desirable to remove immediately from the room the air which rises about the lamp, carrying with it products of combustion, and this was accomplished by placing a hood above the lamp with a pipe leading to a ventilating outlet. That the ventilation was sufficiently good is shown by the fact that lamps burned continuously for several hours showed no decrease in intensity, and that a complete change of the air (obtained by placing a fan in an open window and blowing outdoor air through the room) caused no perceptible increase of candlepower. In the work of Butterfield, Haldane and Trotter, however, where the ventilation was insufficient, measurements of the carbon dioxide were regularly made as a test for the condition of the air, and corrections for vitiation were made; their value for the humidity coefficient is larger than that obtained either at the Bureau of Standards or at the Reichsanstalt, where such correction was unnecessary.

5. COMPLETE EQUATIONS FOR HEFNER AND PENTANE LAMPS

In reducing to normal conditions the data discussed in the following pages, the coefficients given by Liebenthal have been used for the Hefner lamps, while for the pentane the officially adopted formula has been modified by the substitution of our own value (0.0057) for the water-vapor coefficient. The equation for the Hefner lamp is then

$$I = I_n [1 + 0.0055\ (8.8 - h) - 0.00011\ (760 - b)]$$

and that for the pentane lamp is

$$I = I_n [1 + 0.0057\ (8.0 - h) - 0.0008\ (760 - b)]$$

where I is the observed candlepower of the lamp under the given atmospheric conditions; I_n is the normal value of the lamp, that is, its candlepower at an atmospheric humidity of 8.8, or of 8, liters of water vapor per cubic meter of air, and a barometric pressure of 760 mm of mercury; h is the number of liters of water vapor per cubic meter of air, as found by the Assmann psychrometer; and b is the barometric pressure in millimeters of mercury.[10]

I_n is not assumed for either Hefner or pentane lamps, but is the quantity to be determined by each measurement. Putting A and B for the two correction terms,

$$I = I_n\ (I + A - B),$$

or

$$I_n = \frac{I}{I + A - B}$$

In accordance with this equation a value for I_n is calculated from each observed value for I, and in judging the performance of a lamp it is important to find how closely these different values for I_n for a given lamp agree with other, whether the average values of I_n found for different lamps of the same type are the same, and whether the value found for lamps of a given type is the nominal one, namely, 10 candles for the pentane lamp and nine-tenths of a candle for the Hefner.

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[10] The coefficients 0.00011 and 0.0008 apply only to pressures near the normal; for higher pressures the variation is less and for lower pressures greater. When the investigations now in progress at the Bureau are completed we shall probably change the coefficient for the pentane lamp to 0.0006 at normal pressure.

III. OBSERVATIONS ON THE SEVERAL TYPES OF LAMPS

1. WORKING STANDARDS USED

The measurement of the flame standards in terms of the fundamental electric standards of the Bureau, which are 16 candlepower carbon lamps burned at 4 watts per candle, involves a comparison between lights of marked difference in color, except in the case of the Carcel. For both pentane and Hefner lamps this difficulty is very serious, the case of the Hefner being worst of all, not only because it is reddest but also because it requires a larger step down in intensity, which of itself is difficult to make with accuracy. For this investigation sets of electric working standards were calibrated at voltages below the normal, chosen to make the lamps match the flames in color. The heterochromatic measurements were thus confined to the calibration of these standards, and in the measurements of the flames variations due to color difference were avoided. Any uncertainty in the calibration of the electric working standards is, of course, carried over into all the values obtained for the flames. The questions of heterochromatic photometry involved need not be discussed here, but it is not probable that the results obtained by other groups of observers would differ by more than one-half per cent from that used in the case of the standards calibrated to match the pentane flame. For those which match the Hefner flame the uncertainty is greater, and differences of 1 per cent might occur between independent calibrations.

2. THE CARCEL LAMP

In the discussion of correction coefficients no mention has been made of the Carcel lamp, because its performance is so erratic that no one has been able to determine any of its coefficients. Very few measurements on the lamp have been made at the Bureau, but those made have confirmed the conclusions reached by other observers in that the lamp never does reach a steady state, the intensity in different directions and with different chimneys varies considerably, shifting the chimney up or down a small distance often changes the candlepower by several per per cent, and the departure of any one measurement from the mean value of the lamp is likely to exceed 2 per cent when the utmost care is taken to reproduce the conditions of burning. While the mean candlepower obtained happened to fall very near the normal value (9.62 international candles), no confidence could be felt in any value so determined, and it appeared useless to spend more time on the lamp.

3. THE HEFNER LAMP

The Hefner lamp has had a long and honorable career. Although it has some serious defects and requires much patience and skill and many observations to obtain accurate results, it nevertheless has some important merits. If it had not, it would not now be contesting for first place among primary flame standards, after the world has had more than a quarter of a century in which to replace it by a better one.

Its principal merits as a primary standard are its simplicity of construction and operation, ease of manipulation, portability, durability, and the excellent agreement of one lamp with another. Its defects are its small intensity, unstable flame, reddish color, and the difficulty of setting the flame at exactly the right height. For either a primary or a secondary standard these, it must be admitted, are serious objections.

The Reichsanstalt certifies Hefner lamps as correct if within 2 per cent of their standard. At the Bureau of Standards we have eight Hefner lamps—four made by one company and four by another—and all fall within this limit. Indeed, the maximum departure of any lamp from the mean of all is scarcely more than 1 per cent. However, a primary photometric standard is not entirely satisfactory so long as appreciable differences exist among a lot of lamps made to the same specifications. Accidental errors will, of course, occur in the measurements, but of these eight Hefner lamps, certain ones are regularly high and others regularly low, showing that the lamps are not as nearly identical in construction as they should be. This result is due to two things. In the first place, the specifications are not as precise as they should be, and in the second place there are in some lamps slight departures from the specifications. That the intensity of the flame may always be the same—under the same atmospheric conditions—it is necessary (1) that the fuel be uniform, (2) that the wick tube shall always be of the same material and dimensions, and (3) that the height of flame be constant. In comparing lamps, the same fuel and the same kind of wick are used in the different lamps, and comparisons are made with the same apparatus and practically in the same atmosphere, as they are used in succession by the method of substitution. Hence the differences observed are due (1) to differences in flame height or (2) to differences in the effect of the wick tubes on the size or temperature of the flame.

There are two styles of sight used on Hefner lamps. The earlier form has a horizontal plate, 0.2 mm thick in the center of the sight tube, and the height of the flame is adjusted until sighting along this plate one sees the tip of the flame in the correct position with respect to the plate. In the other form, due to Krüss, the flame is projected by a lens upon a ground-glass screen, and the tip of the flame is made to fall on a line across the center of this screen. This is the more convenient and preferable form. The eye is fatigued by the naked flame viewed through the first form of sight, and the adjustment can not be made as accurately to the plate as to the line on the screen in the second form. A slightly higher average candlepower is obtained for the lamps having the Krüss sight than for those having the Hefner sight. The authors recommend the use of the Krüss sight only, and for these three separate reasons: (1) It is less fatiguing to the eye, (2) it permits more consistent settings, (3) it makes possible a higher degree of reproducibility by avoiding whatever difference there may be due to using two forms of sight. When it is remembered that 1 mm change in flame height represents 2 per cent change in flame intensity, and hence the allowable error is only a few tenths of a millimeter in the position of the nearly nonluminous tip of the flame, it is seen that this adjustment is one which requires great care and experience, and an optical device for a sight that is accurately reproducible. Unfortunately, this setting at best is not wholly free from personal equation.

The flame gauge is satisfactory and permits a very close reproducibility in setting the wick tube with respect to the sight. The gauges could, however, be made somewhat more accurately than they are, since several of those examined were in error by two tenths per cent.

The wick tube affects the flame in several ways. The bore should be 8 millimeters exactly, and this determines to some extent the size of the flame. This dimension is very accurately met in all the lamps. The thickness of the tube is specified to be from 0.14 to 0.17 mm. The tube conducts heat down to the liquid amyl acetate which saturates the wick, the top of which is from 1 to 3 mm below the top of the tube, but it also conducts heat on down to the body of the lamp and dissipates more from its surface. The thicker the tube the more readily is the heat conducted, and hence with the thicker tube the top of the wick must be higher in the tube to give the correct flame height. Also, the thicker-walled tube cools the flame more, and therefore reduces its candlepower. Hence, the wick tube should be very accurately specified to insure reproducibility. A departure of one or two hundredths of a millimeter from the mean in the thickness of the wall of the wick tube might seem negligible, but its effect is not negligible. To insure strict reproducibility, the weight of the tube should be specified in addition to its bore and its length; the composition of the German silver of which the tube is made ought also to be specified, to insure uniform results. There is reason to believe that if the specifications were drawn closer and the construction were as exact as it might be, a considerable improvement in the reproducibility would result.

The fuel, amyl acetate ($C_7H_{14}O_2$), is readily obtained pure enough to satisfy the specifications. We have, however, received from a reputable chemical firm amyl-acetate which was guaranteed by them to be pure, which did not conform to the specifications, and which gave a flame of slightly different intensity from amyl-acetate fulfilling the specifications. Hence, the only safe way in precise work is to test the fuel before using it, or purchase only amyl acetate that has been tested with reference to its use in the Hefner lamp.

The flame height specified in the Hefner lamp is 40 mm, at which height it gives nine-tenths of an international candle. An extended study has been made of the amyl-acetate lamps when burning at a flame height of 45 mm, at which height they give one international candle; at least those with Krüss sights give, on an average, one international candle. Taking the mean of all, the height should be about 45.25 mm. It is believed, however, that when the wick tube is more accurately specified, and the Krüss sights alone are employed, a flame height of 45.0 mm will give very accurately one international candle.

There is no appreciable temperature-light coefficient to the Hefner lamp between the limits of temperature that are commonly employed. It is, however, steadier at from 15° to 20° C than at higher temperatures. Hence, for work of highest precision a comparatively narrow range of temperature might well be specified.

In Table 5 is given a summary of results obtained on eight Hefner lamps, two of which, however, are new lamps and have been compared only a few times. Of the remaining six, three have the Hefner sights and three the Krüss sights. In the first part of the table the results are given for a flame height of 40 mm and in the second for 45 mm. In the second column is given the number of measurements made on each lamp, a "measurement" being the value found on a given occasion as the mean of 20 or more separate settings on the photometer and two to five new adjustments of the flame. More than half of the measurements were made by Mr. Crittenden and Mr. Taylor, while the others were made by various persons of less experience with flame standards. For comparison, the results obtained by the more experienced observers are given separately.

TABLE 5

Summary of Measurements on Eight Hefner Lamps

Lamp	Weight of wick tube in grams	Flame 40 mm high				Flame 45 mm high				Percentage of mean deviation from mean cp	
		All measurements		B. C. C. & A. H. T.		All measurements		B. C. C. & A. H. T.			
		No. of meas.	Mean cp int. candles	No. of meas.	Mean cp int. candles	No. of meas.	Mean cp int. candles	No. of meas.	Mean cp int. candles	40 mm	45 mm
Hefner sights:											
804 K	1.246	21	0.889$_7$	15	0.890$_7$	17	0.990$_7$	11	0.992$_6$	0.74	0.66
879 S-H	1.145	19	0.897$_3$	13	0.898$_6$	17	0.991$_0$	11	0.993$_7$	0.50	0.65
1342 S-H	1.144	19	0.896$_1$	13	0.897$_3$	17	0.991$_3$	11	0.988$_7$	0.67	0.92
Mean	....	......	0.894$_4$	......	0.895$_6$	......	0.991$_0$	......	0.991$_6$	0.64	0.74
Kriiss sights:											
786 K	1.311	26	0.901$_1$	19	0.901$_1$	23	0.997$_5$	17	0.998$_4$	0.50	0.65
887 S-H	1.153	32	0.907$_5$	20	0.906$_8$	25	1.001$_9$	18	1.001$_3$	0.44	0.47
1343 S-H	1.121	33	0.903$_2$	21	0.901$_8$	24	1.000$_1$	17	0.999$_7$	0.54	0.70
Mean	....	......	0.903$_9$	......	0.903$_2$	......	0.999$_8$	......	0.999$_8$	0.49	0.61
Mean of all	....	......	0.899$_2$	......	0.899$_4$	......	0.995$_4$	......	0.995$_7$	0.56	0.68
New lamps:											
1714 K	1.177	5	0.890$_8$	4	0.887$_1$	......	....	......	....	....	....
1715 K	1.184	5	0.896$_8$	4	0.895$_1$	......	....	......	....	....	....

The numbers given above for the several lamps are the numbers placed upon them at the Physikalisch-Technische Reichsanstalt, where all were tested and certified. The letters following the numbers indicate the maker.

The mean value of the first three lamps at 40 mm flame height (to three decimal places) is 0.896, and of the second three 0.903, the mean of the six being 0.899 international candles. This is very near indeed to the value 0.900 international candles, assigned to the Hefner lamp in the international agreement of 1909; in fact, it is nearer than one can expect to repeat the determination, because of the difficulties of color and intensity mentioned above.

The mean value of the first three lamps at 45 mm flame height is 0.992, and of the second group of three is 1.000, the mean of all being 0.996 international candles. This is very near, indeed, to one international candle. As the different lamps vary in candlepower on account of slight differences in their dimensions, the agreement between lamps can be improved, and when the closer specifications are drawn they should be so fixed as to make the candlepower at 45 mm as near as possible to one international candle.

The average difference of the separate measurements from the mean of all, for each lamp, is given in the last columns of the table, for the measurements of the more experienced observers only. They average 0.64 and 0.49 per cent, respectively, for the two groups of lamps at 40 mm, or 0.56 per cent for all. At 45 mm the average is 0.74 and 0.61 per cent, respectively. That is to say, a single "measurement" is in error on the average a little more than one-half per cent. In the case of lamp No. 1,343 at 40 mm, the 21 measurements were divided into three groups of seven each. Calling the mean of each group of seven measurements a determination, we find—

	International candles.	Difference from mean.
First determination	0.8997	0.0021
Second determination	0.9017	0.0001
Third determination	0.9049	0.0031
Mean	0.9018	
Average		0.0018

Thus, each determination differs from the mean of the three by two parts in a thousand. If the lamp should continue to do as well, and other lamps could be made to agree with it accurately, this would be a very good performance for a primary standard. No reason is known why the lamp should not continue to do as well, nor why different lamps may not be made to agree much better than heretofore. Since the chief differences in the lamps are believed to be due to the wick tubes, it is mainly a matter of careful construction and painstaking inspection, wherein all tubes not conforming to strict specifications are rejected. Then if each lamp has three or more tubes, all of which are used in succession, and the mean of the results taken, the accidental unavoidable errors in the tubes will be largely eliminated. If the Hefner lamp were to be adopted as a primary photometric standard, it would be advisable to specify further that the mean value of at least three lamps, each supplied with three tubes (at least 10 determinations being made with each tube), be taken as the value of the unit.

In the above table, the lamp in each group that has the lowest candlepower has the thickest (and heaviest) wick tube. Both are from the same maker and both have the flame gauge 0.2 per cent too short. The high values of No. 887 are also due in part to an incorrect gauge, in this case 0.2 per cent too high.

The results shown above are better than have been obtained heretofore at the Bureau and illustrate what can be done by experienced observers working under the most favorable conditions, As a working standard under ordinary conditions, much greater errors would, of course, be found.

4. THE PENTANE LAMP

The Harcourt pentane lamp presents a striking contrast to the Hefner. It is bulky, relatively complicated in construction, less portable, and less convenient in manipulation, more expensive in first cost and in fuel, and requires much better ventilation and a larger photometer room. On the other hand, its higher candlepower, steadier flame, and better color are very great advantages. As to reproducibility, it is easier to reproduce results with a given pentane lamp than with a Hefner lamp when both are operated under correct conditions, but there is a greater difference among different pentane lamps than among different Hefners.

No wick is used in the pentane lamp. The fuel (pentane, C_5H_{12}) is contained in an elevated reservoir or saturator. Air enters the inlet and mixes with the vapor of pentane as it passes over the liquid pentane through the maze into which the saturator is divided by vertical vanes, and this mixture flows down the supply pipe to the burner. In hot weather the pentane may evaporate so rapidly as to flow out through the inlet, and thus prevent the air from entering. In this case, only pentane vapor is fed to the flame. Air, heated by passing through the annular space between the inner and outer chimney, flows down through the hollow standard and into the central chamber below the burner. Thus the flame resulting from the combustion of the vapor of pentane as it issues from the ring of 30 holes in the steatite burner is fed with preheated air within the flame. while it takes atmospheric air directly through its outer surface. The length of flame used is determined by the distance between the burner and the chimney, which is adjusted to be 47 mm when cold, and the height of flame is controlled by the rate of supply of the fuel. The latter is regulated by a stopcock. The tip of the flame is viewed through a mica window in the lower end of the inner chimney, and must be watched and frequently regulated in work of the highest precision. When the flame is at the correct height its candlepower is a maximum. As in the case of the Hefner, the intensity of the flame depends upon the dimensions of the lamp, the composition of the fuel, the atmosphere in which it is burned, and the manipulation of the lamp, especially as regards regulating the flame height and screening the flame.

The specifications of the standard pentane lamp were carefully drawn, and have been closely followed by the several makers of the lamps, with, however, some variations in the American lamps. But that the specifications are not sufficiently exact and complete is shown by the fact that different lamps differ in candlepower appreciably. That is, different pentane lamps burning the same fuel, in the same atmosphere and operated by the same people, differ by as much as 2 or 3 per cent, quite independently of the errors of observation. It is not possible, therefore, to take the light of a pentane lamp as 10 international candles under the stated standard conditions. It may in any particular case be only 9.6 or 9.8 candles at standard humidity and barometric pressure, even when the fuel and all external conditions are right.

The total intensity of the light of the flame depends, of course, on its dimensions, and this is affected by the size of the burner. The specifications say that there shall be 30 holes (from 1.25 to 1.5 mm in diameter) drilled in a circle in the steatite burner, the outside and inside diameter of which are 24 mm and 14 mm, respectively. But the precise diameter of the ring of holes is not specified, and this is found to vary in different burners.

Of the three English lamps for which values are given in this paper all fulfill the specifications regarding burners, and all have the individual holes about the same size (1.35 mm in diameter), but in the one which gave the low candlepower the diameter of the circle of holes was 2 per cent smaller than in the others. This was thought to be a possible explanation of the low value, but it has since been found that the effect on the candlepower does not exceed 0.5 per cent. A series of interchangeable burners, in which the variations were made even greater than the specifications permit, have been tested. In these the outer diameter of the circle of holes varies by 4 per cent, and the different burners have holes ranging from 1.1 mm to 1.5 mm in diameter; the combined effect of variation in holes and in size of circle is only about 1 per cent in candlepower. The reason that this effect is so small is probably to be found in the fact that the pressure on the vapor is very small, and the flow from the holes is so gentle that the vapor spreads so as to cover the whole top of the burner. Consequently, the size of the flame is determined more by the size and shape of the top of the burner than by the dimensions and location of the holes in it. Still, a closer specification of the latter would remove a source of small differences between lamps.

It is well known that a pentane lamp increases in candlepower for a time after lighting up, and that one should wait from 15 to 30 minutes before taking measurements. In Fig. 5 are given four curves taken during the heating-up period of the lamp, showing that the light increases to a maximum and then decreases to its steady value. This maximum is from 1.5 to 3 per cent above the final value, which is reached in from 15 to 30 minutes. The first two curves are for English lamps, which reach a steady condition in half the time required by the early American lamps whose performance is shown in the lower curves. These American lamps were of the type first made in this country, which had lower candlepowers than most English lamps, and the study of these heating curves led to the discovery of one cause of the low candlepower. The form of the curves indicates the presence of two opposing influences, one tending to make the candlepower high and the other, which becomes effective a little later, tending to lower the candlepower. In the American lamp this second effect is greater than in the English form. These two opposing influences are simply the temperatures of the two columns which constitute the circulatory air system of the lamp. The chimney becomes hot first and a vigorous circulation is set up, making a strong draft up through the burner and thus broadening the flame. As the lamp standard, through which the air flows down, becomes warmer, the temperature difference of the two columns is less; the circulation is less vigorous, and the flame becomes slightly narrower.

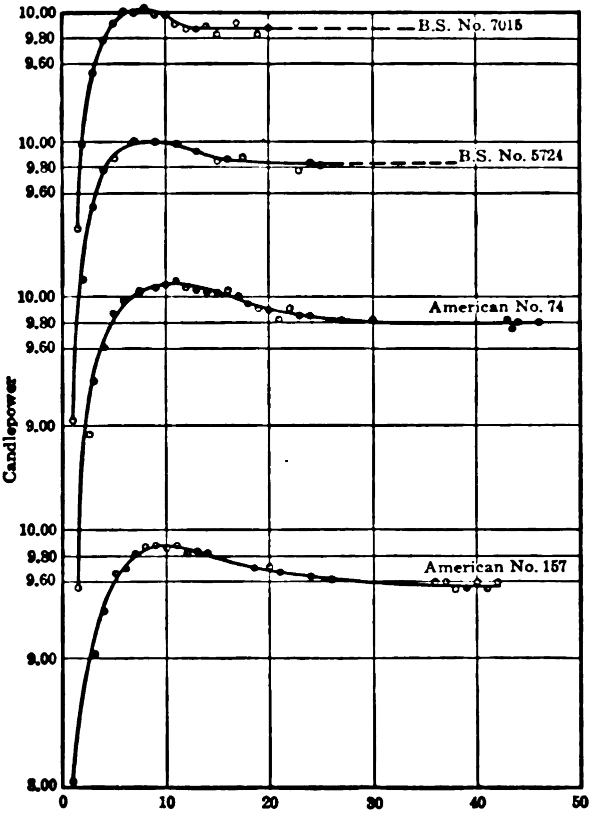

Fig. 5.—*Variation of candlepower of pentane lamps after lighting.*

Beneath the saturator is a flat radiating plate, which in the English lamps is brazed to the standard and serves to conduct heat away, thus keeping down the temperature of the downflowing air. In the early American lamps this plate was considered primarily as a support for the saturator, and it was connected to the standard only by two bands. It therefore failed to function properly as a radiator of heat; the standard became too warm, so that the air flow was decreased and the candlepower lowered. Experimental tests showed that the substitution of a brazed plate for the loose one increased the candlepower by about 1 per cent, while freeing the plate from the standard, even without removing it entirely from the lamp, caused a reduction of the candlepower. In one case, the same American lamp gave 9.63 candles when the plate was not in contact with the standard and 9.75 in the regular condition. This suggests the possibility of an appreciable variation being introduced by accidental change of the contact between the plate and the standard. For this reason, as well as to bring the lamps nearer 10 candles, the brazed plate should be used.

Another detail of construction which makes a measurable difference in the same way is the connection between the bottom of the chimney and the standard. This should be of nonconducting material, but in the first American lamps it was made of metal, which conducted heat across to the standard and thereby reduced the candlepower. When these two faults of construction are remedied, as they have been in more recent lamps, the American form will reach a steady state in about 20 minutes after lighting. The newer lamps also give higher candlepowers than those shown in this paper.

By interchanging parts so far as possible, evidence has been obtained that the discrepancy between the English lamps studied is largely due to some difference in the air system, but, unfortunately for this work, the lamps are not intended to be taken apart and the parts are not interchangeable in general. Consequently the exact cause of the difference has not been found.

The candlepower of a pentane lamp can be appreciably increased by any method of cooling the standard. Even the introduction of a screen to cut off the radiation of heat from the flame to the standard makes a perceptible difference, and drafts of air blowing over the lamp probably produce more effect through the disturbance of temperature conditions than by disturbing the flame directly. Precautions should therefore be taken to obtain a gentle and regular flow of air past the lamp when it is in use.

There is one feature which tends to make the American lamp higher in candlepower than the English form. This is the method of supporting the inner chimney. The chimney is set, when cold, 47 mm above the burner, but the expansion on heating reduces the height. Since the chimney is supported near the bottom in the American lamp and at the top in the English, the reduction in height is less in the former type. The actual height when the lamps are burning has been found to be 46.7 mm in one American lamp and 45.9, 45.8, and 45.7 mm, respectively, in three English lamps. Incidentally these variations suggest that if the lamp is to be a primary standard some better method of fixing the height is necessary.

Although many lamps of English and of American manufacture have been tested, none of them except a few very recent American lamps have shown a candlepower as high as that of the standard pentane lamp of the National Physical Laboratory. The maker of that lamp, from whom the bureau purchased two lamps, was unable to duplicate it exactly as to candlepower.

One of the difficult features of the use of pentane lamps is the fuel. In addition to the inconvenience of pentane being very volatile and explosive, its composition is variable, and as sometimes supplied does not conform to specifications. It is distilled from gasoline, its composition being made nearly uniform by repeated distillation. Besides the great difficulty in separating all the butanes (C_4H_{10}) and all the hexanes (C_6H_{14}), pentane itself (C_5H_{12}) exists in three separate forms, which have different boiling points. Two of these come within the range of temperature used in the final distillation, and in addition the distillation carries over more or less of the substances which have higher boiling points. Hence if pentane which complies strictly with the specifications be distilled it may be separated into three portions of appreciably different boiling points. This fractionation goes on in the saturator, and the photogenic value of the pentane changes to an appreciable extent in a few hours. The official specifications of the London Gas Referees direct that the residual pentane be emptied out of the saturator at least once in each calendar month. For work of the highest precision the authors find that it is desirable to do this every time the lamp is refilled, and that this refilling be done frequently, not waiting until the pentane is nearly exhausted. This requires the rejection of a considerable fraction of the pentane. For less precise work, such as ordinary testing, it is allowable to use a larger portion of the pentane, but even then it is better to make correction when the heavier fractions are used. This correction is discussed in the paper on the use of the pentane lamp to which reference has been made.

In Table 6 are given the results of candlepower measurements made upon three English and four American pentane lamps. In the second column is given the number of measurements made on each lamp from which the mean value has been computed. As with the Hefner lamp previously discussed, a "measurement" is the mean of a large number (30 or more) of individual settings on the photometer, the flame being inspected (and adjusted, if necessary) several times during the set. A group of 30 settings (constituting one measurement) on the pentane lamp is made in about 5 minutes, whereas a group of 20 settings on a Hefner lamp requires on an average about 15 minutes. The difference is due to the much greater unsteadiness of the Hefner flame, which often requires waiting for the flame to be steady and at the right height; whereas, with the pentane, settings are made in rapid succession. The method employed of automatically recording the photometer settings makes rapid settings practicable in the most precise work. The average deviation of a single measurement from the mean of all is given for each lamp in the fourth column, and amounts to a little less than 0.4 per cent on the average.

TABLE 6

Measurements of Pentane Lamps, Apr. 8 to Sept. 9, 1910

Lamp	Number of measurements	Mean candlepower international candles	Mean deviation from mean candlepower
Chance, No. 116	220	9.875	0.03_9
Chance, No. 118	81	9.89	0.02_8
Sugg, No. 171	165	9.62	0.03_8
American, No. 25	42	9.61	0.04_5
American, No. 74	43	9.73	0.03_9
American, No. 157	46	9.58	0.04_1
American, No. 162	31	9.80	$0\ 02_6$

In Table 7 are given the separate measurements in sets of 10, each group constituting a "determination" of candlepower, for four pentane lamps. This shows the order of magnitude of the deviations of each measurement from the mean of a group. These variations are due to a considerable number of factors, such as variation in the atmosphere, in the fuel, in the effects of drafts and of flame adjustment, as well as errors of the photometric measurements.

TABLE 7

Separate Measurements of Candlepower for Two Pentane Lamps

AMERICAN LAMP, NO. 25

9.64	9.67	9.61	9.56
9.59	9.67	9.61	9.62
9.63	9.75	9.62	9.58
9.65	9.70	9.64	9.64
9.53	9.65	9.63	9.64
9.53	9.64	9.56	9.62
9.53	9.63	9.57	9.64
9.46	9.62	9.60	9.56
9.46	9.60	9.65	9.60
9.50	9.57	9.59	9.64
9.552	9.650	9.608	9.610
Mean of all—9.605			

AMERICAN LAMP, NO. 157

9.60	9.57	9.62	9.53
9.63	9.61	9.64	9.65
9.64	9.61	9.47	9.61
9.61	9.55	9.48	9.60
9.61	9.59	9.51	9.57
9.58	9.58	9.51	9.64
9.60	9.58	9.52	9.62
9.61	9.59	9.51	9.58
9.61	9.62	9.54	9.62
9.57	9.64	9.53	9.54
9.606	9.594	9.533	9.596
Mean of all—9.582			

In Table 8 the results are given of different determinations on four American pentane lamps. In the columns headed △ are the differences from the mean, which average 2 parts in 1000 for all the determinations of candlepower on the four lamps. The error in the mean would, of course, be less than this if the lamps are as consistent with themselves as they appear to be.

TABLE 8

Determination of Candlepower for Four American Pentane Lamps

Determination	Lamp No. 25		Lamp No. 74		Lamp No. 157		Lamp No. 162	
	Int. candles	Δ	Int. candles	Δ	Int. candles	Δ	Int. candles	Δ
1	9.552	−0.053	9.675	−0.052	9.606	+0.024	9.796	−0.004
2	9.650	+0.045	9.754	+0.027	9.594	+0.012	9.807	+0.007
3	9.608	+0.003	9.734	+0.007	9.533	−0.049	9.797	−0.003
4	9.610	+0.005	9.744	+0.017	9.596	+0.014	....	....
Mean	9.605	0.026	9.727	0.026	9.582	0.025	9.800	0.005

In the above table Δ is the difference between a single determination and the mean of the several determinations given in the table. A "determination" is the mean of 10 "measurements."

In Table 9 are given similar results of a larger number of determinations on three English pentane lamps. The 22 determinations on the first Chance lamp represents 220 measurements, or probably about 10 000 separate photometric settings. The average value of the deviations of the separate determinations from the mean of all is 2 in 1000 for two lamps, and 1.3 for the third. If the determinations on each lamp be divided up into groups of four, the mean of each group differs from the mean of all by only one-tenth of 1 per cent. This is a gratifying degree of reproducibility. Of course, such results would be obtained only as the means of a considerable number of measurements, even if the flame standards were ideal in their performance, for the errors of the photometric measurements are considerable. That the errors belonging to the flame standards themselves could be so small when measured in all kinds of weather, with a wide range of humidity and temperature, and considerable range of barometric pressure, with many resettings of the lamps, and over a period of some months, we would not have thought possible when this work was begun.

But while the value of a given lamp can be determined with so little uncertainty, the differences between lamps are very considerable. The candlepower of the Sugg lamp is 2.6 per cent less than that of the Chance lamps, whereas two American lamps are slightly smaller in candlepower than the Sugg lamp. It is recognized in England that different pentane lamps differ in candlepower, so that the standard of the National Physical Laboratory is not that of any pentane lamp taken at random, nor the mean value of a group of lamps, but a particular pentane lamp. It remains to learn how to make different lamps agree as closely as a particular lamp will agree with itself, as was remarked above.

TABLE 9

Determination of Candlepower for Three English Pentane Lamps

Determination	Chance, No. 116		Chance, No. 118		Sugg No. 171	
	Int. candles	Δ	Int. candles	Δ	Int. candles	Δ
1	9.821	−0.054	9.880	−0.011	9.585	−0.031
2	9.827	−0.048	9.876	−0.015	9.587	−0.029
3	9.846	−0.029	9.933	+0.042	9.612	−0.004
4	9.875	0.0	9.889	−0.002	9.579	−0.037
5	9.910	+0.035	9.884	−0.007	9.590	−0.026
6	9.894	+0.019	9.882	−0.009	9.599	−0.017
7	9.880	+0.005	9.902	+0.011	9.644	+0.028
8	9.911	+0.036	9.884	−0.007	9.616	0.0
9	9.870	−0.005			9.620	+0.004
10	9.903	+0.028			9.646	+0.030
11	9.895	+0.020			9.614	−0.002
12	9.907	+0.032			9.668	+0.052
13	9.872	−0.003			9.618	+0.002
14	9.883	+0.008			9.630	+0.014
15	9.847	−0.028			9.610	−0.006
16	9.854	−0.021			9.633	+0.017
17	9.871	−0.004				
18	9.898	+0.023				
19	9.858	−0.017				
20	9.876	+0.001				
21	9.867	−0.008				
22	9.878	+0.003				
Mean	9.875	0.019	9.891	0.013	9.616	0.019

The determinations of the Chance, No. 116, and of the Sugg lamp recorded above were made between April 8 and September 9, 1910, during which period the amount of water vapor per cubic meter of air varied from 4 liters to 27 liters. The determinations of the Chance, No. 118, were made between July 18 and September 9, the range of water vapor being approximately from 14 to 27 liters per cubic meter of air.

5. CONCLUSION

While much remains to be done on the pentane lamp to make it a thoroughly satisfactory flame standard, the authors believe that a much closer agreement between different lamps, and a little higher degree of reproducibility in the same lamp, is possible. For use as a practical standard in photometric measurements, and for use as a primary standard for fixing the unit of light, the same lamp should not be employed, and the specifications should be appreciably different. One would not think of employing an ordinary meter bar for a primary standard of length, or of using an ordinary precision resistance box for the reference standards of a national standardizing institution. No more should one think of using a pentane lamp that is not too good for a gas works or for ordinary photometric practice as a primary standard for fixing and maintaining the unit of light. There should be as much difference here as in other physical standards. Vernon Harcourt has rendered a great service to photometry and to the industries in developing his various pentane lamps, and the authors can not refrain from expressing their admiration for the thoroughness with which he worked in the pioneer days of precise photometry. His lamp has stood the test of use, and after years of criticism it remains the most practical flame standard we have. Nevertheless, the results of this study indicate that, at least as made at present, the pentane lamp can not be considered as a reproducible primary standard, its value in this respect being decidedly less than that of the Hefner lamp. If the principles of the present lamp are to be applied to the development of a primary standard, further improvement is necessary, not only in the construction of the lamp, but in its use as well. Instead of using the ordinary style of lamp, at any temperature and any humidity, with the pentane that satisfies ordinary requirements, there should be a lamp (or several lamps) built to very exact specifications, operated within very narrow limits of temperature and humidity, with pentane satisfying much more rigorous requirements as to density and boiling point, and an atmosphere maintained constant as to oxygen content with great care. With such painstaking procedure the unit of light can be fixed with either the Hefner or the pentane lamp with very considerable precision, sufficient at least to serve as a valuable check on the admirable electric standards now in use. It is with a view of contributing something to the working out of such precise specifications that the work of investigation at the Bureau will be continued.

The authors are under obligations to R. S. McBride for his assistance in the chemical examination of the fuels employed in the lamps, to A. H. Taylor for assistance in all the photometric work and computations, and to G. J. Schladt for similar assistance in the later part of the work.

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